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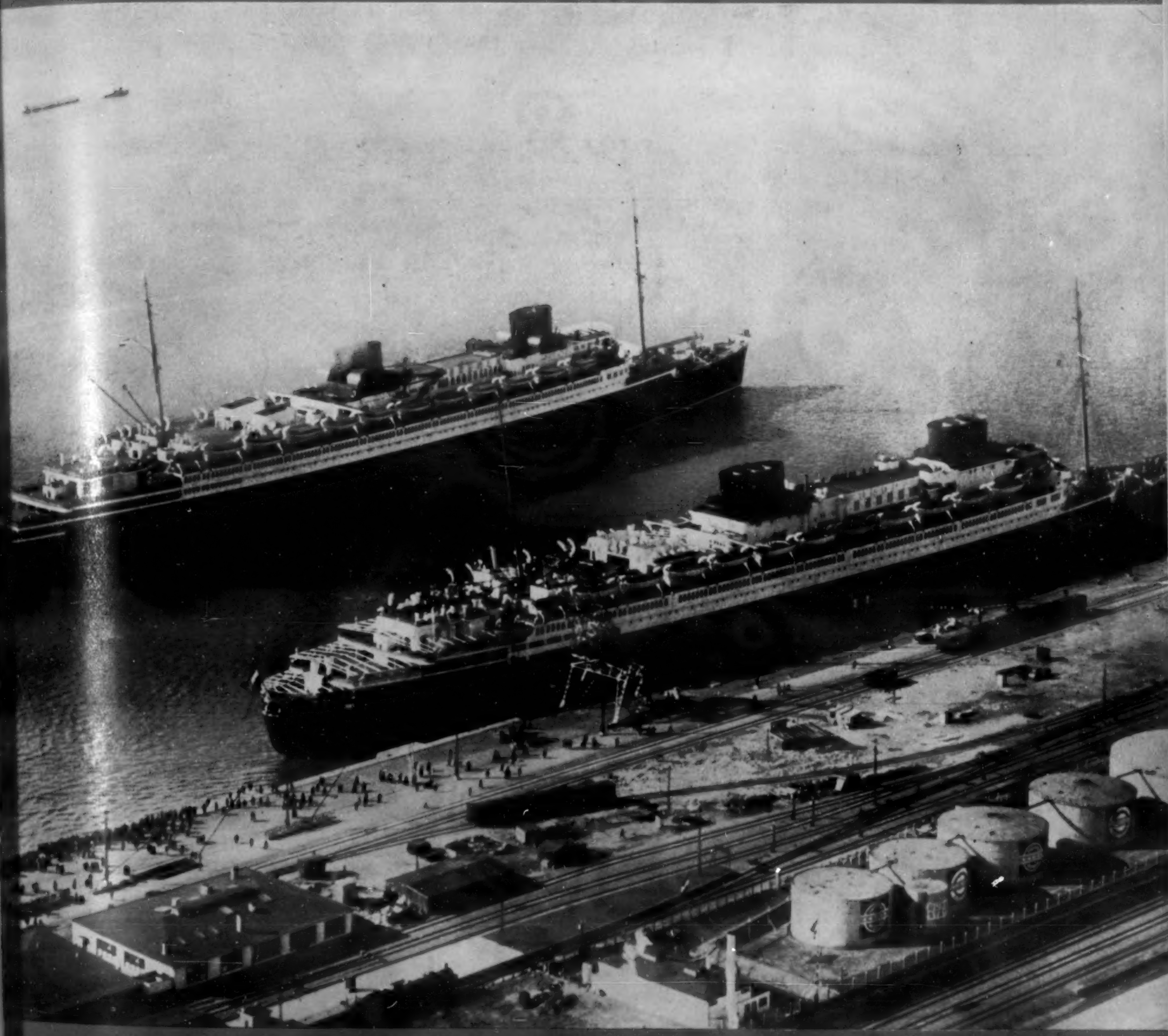
The Magazine of Metallurgical Engineering

INCLUDING

CURRENT METALLURGICAL ABSTRACTS



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METALS & ALLOYS

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CURRENT METALLURGICAL ABSTRACTS

ELECTRIC FURNACES ?
SEE GENERAL ELECTRIC FIRST

See this thing called

COPPER BRAZING

In the G-E copper-brazing process, steel parts are made to grow together by the flowing of molten copper between their tight-fitting joints in a G-E controlled-atmosphere electric furnace.

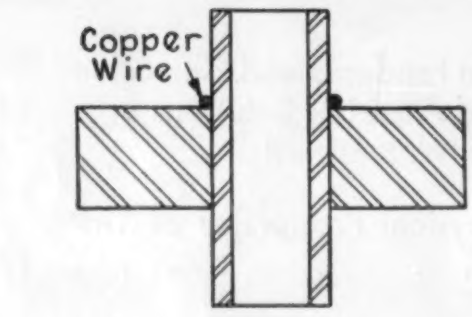


Figure 1

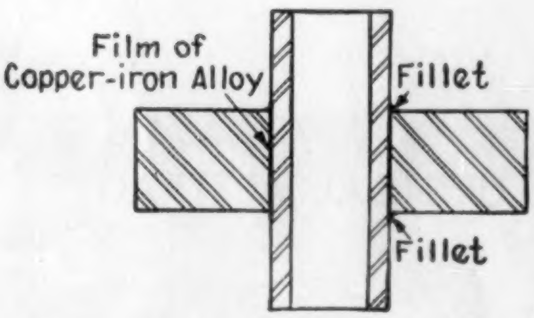
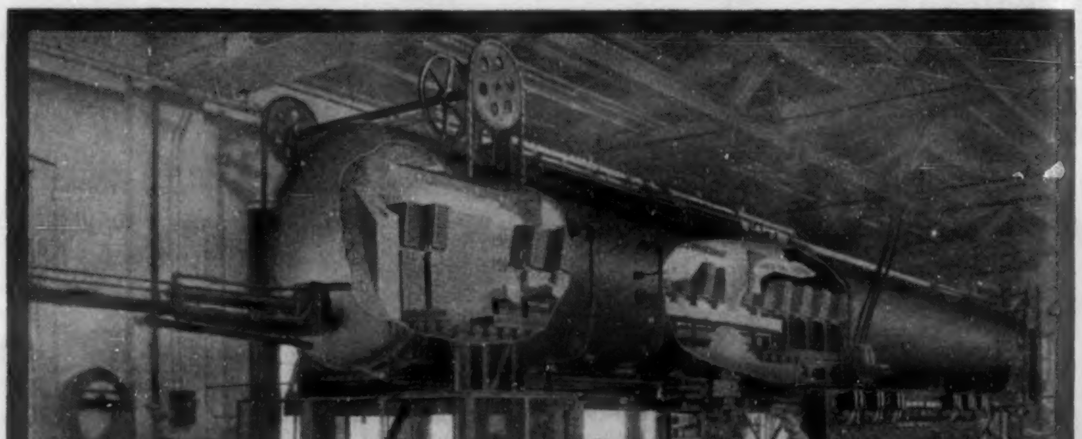


Figure 2

FOR example, note (Fig. 1) a steel tube pressed tightly into a steel disc. A ring of copper wire is placed adjacent to the clean joint. The piece is passed through a G-E copper-brazing furnace. Note the result (Fig. 2). The copper has flowed into the joints by capillary attraction, forming joints stronger than the copper itself. There is also a tendency to grain growth across the joint, which results in remarkable strength.

The potentialities of this process are immense. Every manufacturer fitting together steel parts on a production basis is urged to investigate immediately. Ask your nearest G-E office for complete information and for a copy of Bulletin GEA-1291.



Semicontinuous, pusher-type, copper-brazing furnace for fabricating refrigerator evaporators. The work is placed on conveyor beneath furnace, elevated into furnace, and pushed through

570-179

GENERAL ELECTRIC

SALES AND ENGINEERING SERVICE IN PRINCIPAL CITIES

EDITORIAL COMMENT

Melting High Strength Cast Irons

IT IS ODD that so little interest is shown in this country in respect to a European development that appears well fitted to meet American conditions. We refer to the melting of cast iron in rotating pulverized coal furnaces of the Brackelsberg type.

Scores of accounts of European experience with such furnaces, have been presented at technical meetings abroad in the last few years, and in all the discussion, scarcely a note of criticism has been heard, the general opinion being that they are one of the most important recent advances in foundry practice.

It would appear that they ought to meet with even greater favor here than abroad, since the proportion of alloy cast iron and low carbon, high test iron to ordinary gray iron is greater here. It seems to be well established that the pulverized coal furnace will heat the metal distinctly hotter than the cupola and this is certainly to be desired for low carbon heats. The control of composition seems to be more certain than in cupola melting, and the sulphur pick-up is lower. The quality of the product seems to be distinctly above that of cupola metal and to be more nearly that of the electric furnace product.

The first cost of the furnace and accessory apparatus will, of course, be greater per ton of output, and the refractory costs may be a bit higher. But the interest on the investment and the upkeep should not be excessive, and these charges would appear to be well over-balanced by the saving in fuel cost.

While the cupola, which generates heat by combustion of fuel in actual contact with the charge, is slightly more efficient on the basis of B.t.u. per lb. of metal melted, the cost of foundry coke is roughly twice that of pulverized coal, so there is a big margin of saving on the fuel item.

All in all, it would appear that at no greater over-all melting cost than in the cupola, the pulverized coal system would put the foundryman in shape to handle special irons with a certainty as to quality of product and with a flexibility of operation hitherto obtained only in the electric furnace.

The Brackelsberg furnace obtained a foothold abroad before the world-wide depression, and its flexibility has doubtless helped it to find favor in a period of low and irregular production. Its failure to find recognition here is probably due to hesitation of those who might utilize it to make capital expenditures under recent conditions.

There seems to have been little response to the efforts to introduce it here. Since there are several different makes used abroad of the type of furnace we have referred to as the Brackelsberg, and since pulverized fuel firing and rotating furnaces are old, it would appear unlikely that patent complications could play so large a part as to severely hamper the use of furnaces of that type. One would, of course, be willing to pay something to get the benefit of the experience that has taken the bugs out of a particular design, but there are so few inherent difficulties in the construction and operation of such furnaces that various designs should operate in about the same way.

We believe that there are many foundries not yet ready for electric melting in which pulverized coal melting would offer distinct advantages over the cupola, and we recommended more attention to the subject.

H. W. Gillett

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Good Taste In Non-technical Metallurgical Publicity

THE NON-TECHNICAL public has a real interest in science these days. A handful of writers, more or less versed in science, are catering to this interest by rephrasing scientific developments into everyday language. This activity, on the whole, benefits both the public and the scientist, but it does not benefit either, in the long run, unless the "copy" is true, both as to the facts stated and as to the general impression given. The higher-class writers take pains to check their facts and to make the general impression given by their writings, a true one.

But there are other reporters who see a good story in some scientific stunts and cut loose with little regard to facts. Hence, each year we read of new cancer "cures" on which the flamboyant newspaper publicity varies decidedly from the tone of the accounts of the cancer research published in medical journals. Medical ethics frown severely upon the research worker who connives in the broadcasting of misleading non-technical accounts of alleged "cures." If such accounts are put out prior to scientific publication, scientists will usually class them as, and find them to be, fakes. Medical ethics also bar the research man from claiming vast credit for pioneering when his work merely adds a little to a lot of previous work by others.

Metallurgy is, on the whole, pretty free from misuse of non-technical publicity and from attempts to claim the lion's share of credit when only a mouse's share is due. Once in a while, however, some reporter or some misguided publicity agent pulls a boner so bad that it tends to convey an impression that metallurgical ethics are of a low order.

The scientist classes non-technical accounts of the "rediscovery of the lost art of hardening copper" as quite on a par with those of "cancer cures," and they crop up about as often. Only recently there was published in a non-technical magazine a write-up dealing with work on "Hard Copper" at a state-supported school, which, while it refers to the "lost art" as a myth,

(Continued on Page 76)

Special Austenitic Steels for Severe Corrosion Resistance

BY JAMES A. PARSONS, JR.* AND EARL RYDER†

IN REVIEWING metallurgical developments of the past decade, one of the most prominent examples of scientific achievement is the austenitic high chromium-nickel steels for corrosion resistance. These steels have attracted the attention not only of engineers and chemists, but of architects and ornamental designers as well. Such alloys represent mixtures containing principally 18-20% chromium, nickel ranging between 8-10%, while varying amounts of silicon, molybdenum and carbon are often included in the specifications according to the properties desired. For corrosion resistance, such alloys have admirably served the semi-chemical field both for heat and corrosion resistance, and also in a few instances in the heavy chemical industries, especially for nitric acid.

In handling sulphuric acid and sulphates, particularly under reducing conditions, these alloys have not proven entirely satisfactory. Many attempts have been made to modify the composition in order to supply users of dilute sulphuric acid with a satisfactory material in the form of castings and rolled products. Similarly weak solutions of hydrochloric acid further intensified with moderate concentrations of ferric chloride, present problems which require modification of the 18-8 composition. It is the intention of the authors to describe the peculiar effects of the presence of the salts of the heavy metals, particularly iron, in sulphuric and hydrochloric acids. Special means of conducting laboratory tests to approximate service conditions have been devised and the results of these experiments tend to verify or extend in some instances current theories relative to intergranular attack. The very nature of these pickling solutions assists materially in explaining how carbide precipitation, dissolution and subsequent diffusion control intergranular corrosion.

*Metallurgist and †Research Chemist, Duriron Company, Inc., Dayton, Ohio.

Requirements of Metals in Pickling Processes

Sulphuric and hydrochloric acids are the usual acids employed in the pickling of iron and steel products. The development of corrosion resistant alloys for such service would be a comparatively simple task if the destructive properties of these solutions were confined to the action of the pure acids only. Unfortunately such is not the case, as the presence of dissolved iron and the use of so-called inhibitors, are contributing factors which must be given careful consideration.

The dissolved iron may be present in sulphuric acid solution either as ferrous or ferric sulphate and the ultimate type of corrosive attack on equipment designed for use in pickling processes is governed by the relative amounts of the two salts present. Ordinary plain carbon steel has its resistance to corrosion (evaluated by weight loss) increased by the presence of ferrous sulphate and decreased when ferric sulphate is present. It is understood, of course, that the order of resistance mentioned is of value only from a comparative point of view as this metal is not considered commercially resistant to such solutions.

Alloys of the 18-8 type are not resistant to hot solutions of sulphuric acid, but certain other modifications (Table I) of these austenitic alloys are unaffected by

Tapping Induction Furnace.

Table I. Resistance of Austenitic Nickel-Chromium Steels to Hot 10% Sulphuric Acid. 80°C.

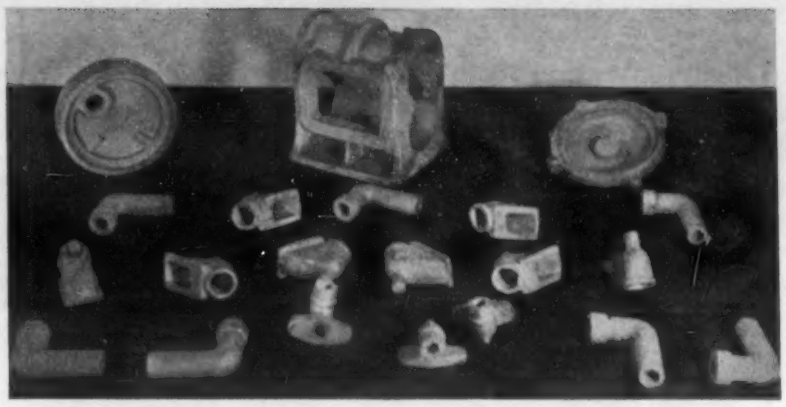
Alloy	Composition						Resistance to Attack by Weight Loss.	
	Ni	Cr	Si	Mo	Cu	Total Carbon	Pure Acid	Acid with low concentration of Ferric Sulphate
18-8	8.00	18.00	0.50	....	....	0.20	Attacked	Attacked
18-8-Mo	8.00	18.00	0.50	3.00	....	0.20	Attacked	Attacked
A	25.00	3.00	5.00	0.70	1.00	0.25	Unaffected	Attacked
D	16.00	2.50	3.00	....	0.50	0.60	Unaffected	Attacked
B	35.00	12.00	5.00	3.00	1.00	0.25	Unaffected	Unaffected
K	16.00	11.00	3.00	....	1.25	0.25	Unaffected	Attacked
L	22.00	21.00	3.00	1.00	0.40	0.25	Unaffected	Unaffected

the pure acids. This is particularly true with the nickel-silicon-copper-iron alloys. In most instances the nickel is considerably greater than the chromium except in the case of the "L" alloy in which case the nickel can be reduced to a value less than the chromium, as shown in Fig. 7.

When the salts of iron are present, the classification of these alloys with respect to resistance to hot dilute sulphuric acid is entirely different. The 18-8 alloys are unaffected when the ferric sulphate content is greater than 1% without any trace of ferrous sulphate. Such a solution is only hypothetical insofar as practical pickling solutions are concerned. The ferric sulphate content seldom runs as high as 1% and when present to a lesser degree it is always accompanied with a concentration of ferrous sulphate far in excess of this value. Ferrous sulphate does not inhibit the action of sulphuric acid on 18-8 alloys so when all factors are taken into consideration, this type of austenitic steel is not satisfactory for sulphuric acid pickling of iron and steel products.

The second column in Table I shows that small concentrations of ferric sulphate (under 1%) increase the rate of sulphuric attack in all alloys except B and L. These alloys have high nickel and high chromium contents. It is interesting to note that silicon and chromium are additive with respect to an oxidizing solution such as sulphuric acid plus ferric sulphate. Both silicon and chromium have high affinities for oxygen and hence tend to build up a stable passive coating. If the alloy contains sufficient nickel and copper to build up resistance to pure sulphuric acid then by adding silicon and chromium in proper amounts the alloy will resist the addition of small amounts of ferric sulphate. It is much better to increase the chromium at a rate greater than the silicon because the latter element causes difficulty in rolling and forging. Thus 21% chromium with only 3% silicon as in L, is much better than 12% chromium with 5% silicon as in B. Additional properties of the nickel-silicon-copper alloys have been fully described by Mathews[1] and Johnson.[2]

Reference has been made to the importance of the combination of chromium and silicon to oxidizing solutions of sulphuric acid. Of no less importance is the combination of nickel and copper in building up resistance to the pure acid or solutions which are highly reducing, that is, containing considerable ferrous sulphate. As a result of a proper balance between chromium and silicon on one hand and an adequate proportioning of nickel and copper on the other, an alloy is obtained such as the "L" composition which has its resistance to sulphuric acid increased in the presence of either ferrous or ferric sulphate or combinations of the two. This is shown by the curves in Fig. 8. The percentage of copper necessary to reinforce the nickel is usually less than 0.50%. With greater amounts no particular advantage is derived from the weight loss view point, while copper plating



Alloy Steel Fittings for Catsup-filling Machine.

results particularly in reducing solutions which is extremely detrimental especially in pickling iron and steel sheets which are to receive light colored finishing coats of Duco, etc. This discoloring effect of corrosion resisting equipment is invariably transmitted to the work being pickled.

The significance attached to the presence of ferric sulphate and its attendant affinity for many corrosion resistant metals and alloys in pickling practice is not overestimated. It is true, that while the pickling operation is in progress, considerable hydrogen is being evolved which tends to reduce the ferric iron. Conversely, the utilization of inhibitors controls hydrogen evolution which has its effect in turn on the amount of ferric that is allowed to remain in solution. Also there are instances where bulky objects such as tanks are being pickled in which case such large volumes of acid are used per unit weight of material that complete reduction is not affected. Sufficient hydrogen in such installations is not generated to maintain ferrous sulphate exclusive of the ferric. Finally some ferric sulphate is in evidence as a result of oxidation in acid splash or the thin films of solution adhering to baskets, hooks, chains, etc., when they are lifted from the tank into the atmosphere. Also during periods of shut-down the salts of iron become oxidized and attack is thereby increased on the equipment before enough hydrogen is evolved in the subsequent run to again reduce the ferric iron.

There are other applications of dilute sulphuric acid corrosion where ferric sulphate attack is of little or no consequence. The handling of battery acid and fumes arising from charging batteries can be handled successfully by means of compositions as shown in Table I.

Methods of Laboratory Testing

Laboratory tests are usually considered merely as rough estimates in determining the suitability of corrosion resisting materials for plant service. This attitude is justified in many instances for the finer points of detailed information relative to dependability are usually assembled after many service trials most of which are unsuccessful. From these preliminary service runs, additional information is obtained which may be used to considerable advantage in improving the technique of future laboratory tests. It is also possible to develop more fully the underlying principles governing the behavior of the actual installation.

Weight loss measurements of special austenitic nickel-chromium steels in sulphuric acid show that the presence of ferric sulphate decreases the attack. This, however, furnished only one-half of the desired information, because ferric sulphate in sulphuric acid has the same effect on these special steels that copper sulphate has in "The Strauss Embrittlement Test," with 18-8 alloys. In the sulphuric acid-copper sulphate tests with this latter alloy the evil effect of precipitated carbides has been

[1] John A. Mathews. *Industrial & Engineering Chemistry,* Vol. 21, Dec. 1929, page 1158.
[2] C. M. Johnson. *Metals & Alloys,* Vol. 1, June 1930, page 547.

Fig. 1. Microstructure of Low Carbon "L" Alloy, ¼ inch hot rolled bar heated at 2250° F. (1235° C.). Etched with "Chrome-Regia." Magnification 200×. (Note large grains and comparatively narrow boundaries).

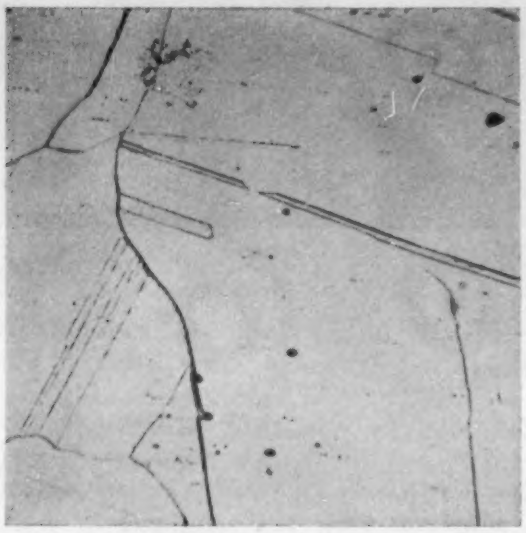


Fig. 2. Complete Carbide dissolution in Low Carbon "L" Alloy, ¼ inch hot rolled bar heated at 2050° F. (1120° C.). Etched with Murakami's Reagent for Carbides and "Chrome-Regia" for structure. Magnification 200×.

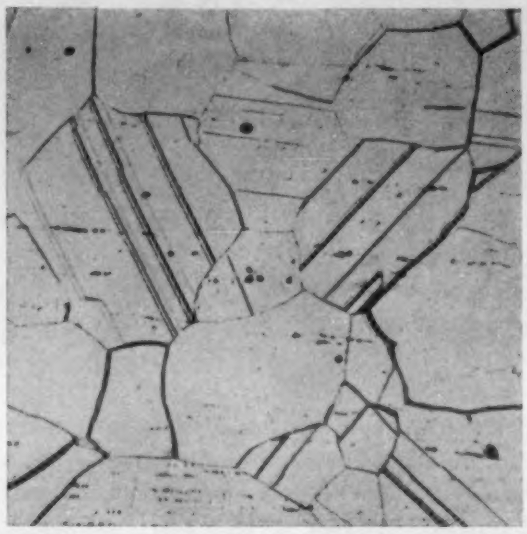


Fig. 3. Carbide precipitation in Low Carbon "L" Alloy, ¼ inch hot rolled bar heated at 1200° F. (650° C.). Specs mostly non-metallic oxides. Etched with Murakami's Reagent. Magnification 200×.

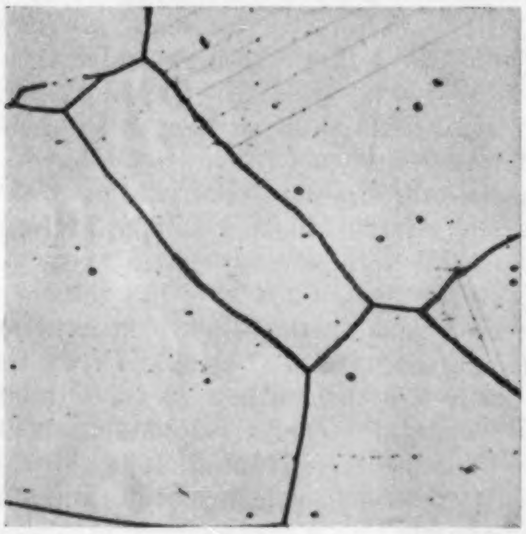


Fig. 4. Microstructure of High Carbon "L" Alloy, ¼ inch hot rolled bar heated at 2250° F. (1235° C.). Etched with "Chrome-Regia." Magnification 200×. (Note large grains and comparatively wide boundaries.)

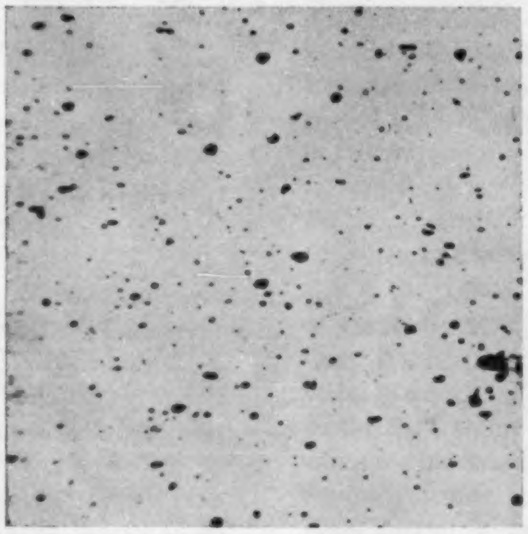


Fig. 5. Partial Carbide dissolution in High Carbon "L" Alloy, ¼ inch hot rolled bar heated at 2050° F. (1120° C.). Etched with Murakami's Reagent. Magnification 200×.

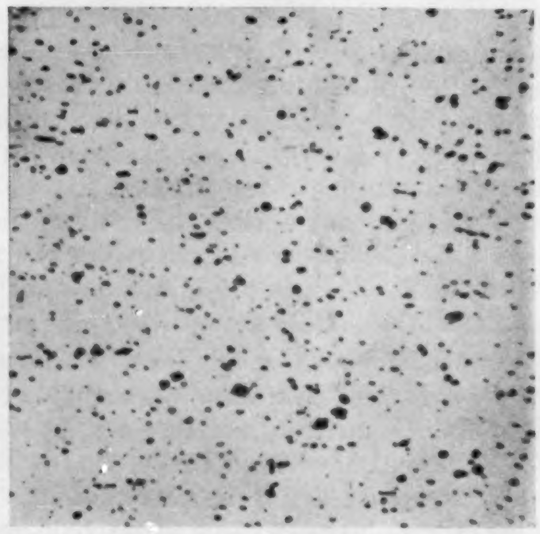


Fig. 6. Carbide precipitation in High Carbon "L" Alloy, ¼ inch hot rolled bar heated at 1200° F. (650° C.). Etched with Murakami's Reagent. Magnification 200×.

thoroughly demonstrated.[3] This solution furnishes a ready means of accelerating the test for 18-8 although its practical application is perhaps more remote. It demonstrates what may eventually occur in other solutions of a similar nature. Ferric sulphate solutions are directly encountered in applications of the special steels and a study of laboratory tests reveals many interesting facts relative to carbide precipitation and dissolution.

Two heat treatments were used in the experiments on a ¼″ diameter specimen of hot rolled rod "L" metal the composition of which is shown in Table I. In the first instance a sample was heated at 1200° F. at the rate of 20 hours per inch of thickness in order to precipitate the carbides. It was later shown, however, that the same rate of corrosion obtains for a shorter period of heating of one hour per inch thus substantiating the contention that carbide precipitation proceeds rather quickly in the temperature range of 1100° to 1400° F. Another specimen cut from the same rod was soaked at 2250° F. for a period equivalent to one hour per inch of thickness. In all heat treatments described in this paper the samples were cooled in still air to room temperature. The solution chosen for the test consisted of a 5% solution of sulphuric acid containing 15% ferrous sulphate. The ferrous salt contained a small amount of ferric sulphate, the analysis of the resulting solution showing about 0.05% of the oxidized sulphate of iron. The composition of the solution ultimately chosen is representative of a typical partially spent sulphuric acid pickling bath. The test was finally accelerated by boiling in an extraction flask under a reflux condenser. Numerous investigators have shown that precipitated carbides deplete the matrix of an amount of chromium equivalent to approximately 16 times the carbon content. The amount of depletion in this case is sufficient to destroy the resistance of the matrix to the corrosive action of the solution resulting in a penetration of 0.340 inches per year as shown in Table II. Other alloys similar in composition, with the exception of carbon are included for comparison.

[3] Charles A. Scharschu. Correct Heat Treatment of 18-8. *Metal Progress*, Vol. 20, 1931, page 68.

Table II. Corrosion of "L" Grade in 5% H_2SO_4 plus 15% Ferrous Sulphate with a trace of Ferric Sulphate.

Heat Treatment 1200° F. at rate of 20 hours per inch of thickness.

No.	Carbon Content	Type of Failure	Time of Test in Hrs.
4	0.04	Intergranular	800
11	0.11	Intergranular	85
13	0.13	Intergranular	54
25	0.25	Weight loss 0.340 inches per year	135

Alloy No. 25 after losing its resistance as a result of carbides robbing the matrix of chromium generated sufficient hydrogen to reduce the small amount of ferric sulphate present to zero. Intercrystalline attack was thus prevented entirely. With alloys 4, 11 and 13 the amount of useful chromium withdrawn by the carbon

was not great enough to lower the resistance of the alloy as a whole. The weight loss is so extremely low that enough hydrogen is not generated to reduce the small amount of ferric sulphate. Intercrystalline attack then proceeds, the time for perceptible attack varying inversely as the carbon content. Carbide precipitation after heat-treatment at 1200° F. occurs within the grains themselves. In a test of this type corrosive attack is mild enough to carefully distinguish between materials containing carbon of slight variation. Thus it is shown that alloy No. 4 is nearly 10 times as resistant as alloy No. 11, and that the increase of two points in carbon of alloy No. 13 over No. 11 shows a vast change in resistance to intergranular attack. Also the presence of an ion in solution of more than one valence, one of which is a criterion of the embrittlement test, serves as a simple means of following the effect of changes in heat treatment on corrosion resistance.

Strauss' work on the heat-treatment of 18-8 alloys emphasized the fact that heat treatment between 1900° and 2100° F. resulted in increased resistance to corrosion by virtue of more thorough dissolving of carbides. Table III shows how heat treatment improves the dissolution of carbides in the special "L" composition, since the specific electrical resistance continually increases with elevation of the soaking temperature. The absence of carbides, permitting a single homogeneous solid solution structure to persist means greater resistivity.

Table III. Effect of Heat Treatment on Electrical Resistivity ("L" Alloy)

Soaking Temperature °F.	Resistivity in Microhms/inch³
1500	41.41
2070	41.78
2250	43.47

Thus it is apparent that heat treatment at temperatures higher than those usually specified (2150° F.) would be advantageous from the viewpoint of more adequate dissolving of carbides. Most austenitic steels of the nickel-chromium type are subject to grain growth at elevated temperatures. In addition to this disadvantage, the carbides upon dissolving, tend to diffuse to the grain boundaries and the rate of diffusion naturally increases with rise in temperature. Since solid solubility and diffusion are so intimately connected, there is little doubt in the coexistence of this phenomena of piling up of carbides at the boundaries following dissolution at high temperatures. Dr. C. H. Herty in his description of Prof. Campbell's researches and M. K. Ziegler's determinations on solubility and diffusion substantiate this relationship.[4] Fig. 1 shows a low carbon (0.04%) material with fairly wide boundaries while Fig. 4 is representative of the 0.25% carbon alloy depicting considerable more piling up of carbides at the boundaries. The heavy grain boundaries are in evidence prior to contact with the corrosive under consideration.

When an alloy such as L-25 (Table II) is heated at 2250° F. at the rate of one hour per inch, cooled in air and tested in the same manner as related for the 1200° F. treatment, no weight loss occurred but the specimen failed from intercrystalline attack in 32 hours. Part of the carbides dissolved prior to diffusion sufficiently to restore a portion of the chromium to the matrix and thus aid the alloy in regaining its corrosion resistance. Intergranular attack resulted because no hydrogen was generated as a result of weight loss to remove the trace of ferric sulphate. It is probably true that only a portion of the chromium in the carbide was returned to the matrix and the balance diffused to the boundaries associated with iron carbides. It is known that at least a portion was restored because the weight loss resistance was maintained and the solution showed its original ferric content on analysis. Alloy L-4 containing 0.04% carbon was not attacked either by weight or intergranular corrosion after 2000 hours of boiling.

Another test which may justly be termed an "embrittlement test" for the special sulphuric acid alloys is a boiling solution of 50% sulphuric saturated with ferric sulphate (approximately 30 grams per liter). Table IV shows the vast difference between the low carbon alloy L-4 (0.04%) and the higher carbon material L-25 (0.25%). This test is exceedingly drastic and is not typical of any commercial pickling solution but it is particularly useful in illustrating the merits of the lower carbon alloy. The specimens described in Table IV were not treated at temperatures sufficiently high to induce grain growth. This indicates that the intergranular attack is a function of either carbide precipitation or dissolution with subsequent diffusion. Also the fact is demonstrated that heat treatment conducted just below the grain growth range considerably improves the alloy but does not compare in any degree with the low carbon mixture even with its small amount of carbides entirely precipitated.

Table IV. Corrosion of "L" Grade in Boiling 50% Sulphuric Acid Saturated with Ferric Sulphate.

Alloy	Heat Treatment	Type of Failure	Time of Test in Hours.
L-4	1200°F (20 hrs. per inch of thickness)	No attack	504
L-25	1200°F (20 hrs. per inch of thickness)	Intercrystalline	20
L-25	2070°F (1 hr. per inch of thickness)	Intercrystalline	96

The ferric chloride content of hydrochloric acid pickling solutions is responsible for the intercrystalline type of corrosion in a manner comparable to sulphuric acid solutions with dissolved ferric sulphate. Similarly 5% solutions of ferric chloride cause embrittlement of the higher carbon alloy with practically no weight loss in a period of a few hours even at room temperature. The phenomena of oxidizing ions in acid solution is again in evidence as a criterion of intergranular corrosion.

[4] Dr. C. H. Herty. *Metal Progress,* Vol. 20, 1931, page 37.

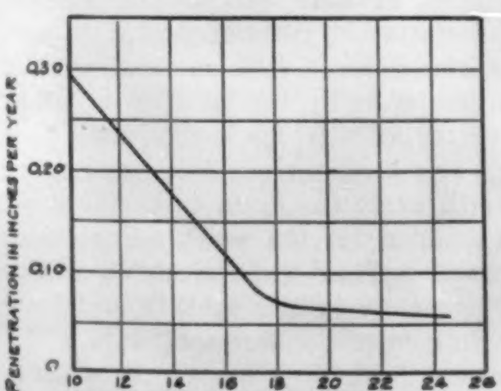


Fig. 7 PERCENT NICKEL
WEIGHT LOSSES IN 10% SULPHURIC ACID AS AFFECTED BY NICKEL CONTENT OF THE SPECIAL AUSTENITIC COMPOSITION

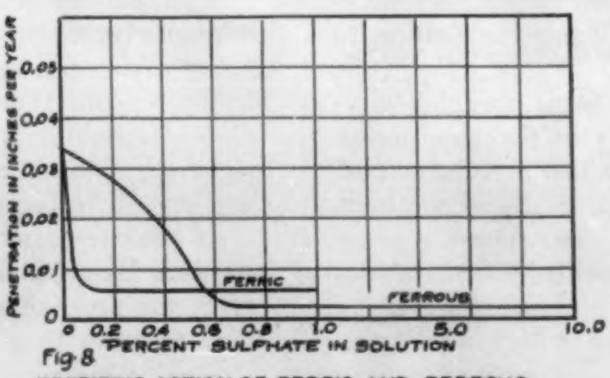


Fig. 8
INHIBITING ACTION OF FERRIC AND FERROUS SULPHATE IN 10% H_2SO_4 ON SPECIAL AUSTENITIC STEEL

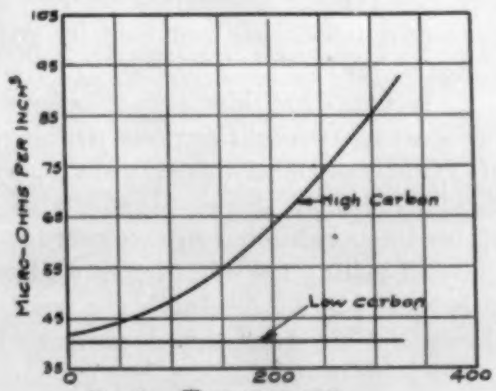


Fig. 9 TIME IN HOURS
ELECTRICAL RESISTIVITY AT VARIOUS TIME INTERVALS FOR SPECIAL NICKEL-CHROME AUSTENICIC STEEL IN A TYPICAL PICKLING SOLUTION

In all tests it was desirable to ascertain with some degree of accuracy the exact time that the samples began to show indications of intergranular attack, in order to successfully evaluate steels of various carbon contents. It is possible to detect intergranular corrosion by dropping the sample on a concrete floor and noting the absence of the metallic ring, but before this type of attack has proceeded far enough to destroy the ring, considerable corrosion has already developed. It is not always convenient to bend the sample in order to detect intergranular attack by brushing away the crystals, therefore, a test was devised and conducted as follows:

The electrical resistivity of the sample was determined prior to immersion in the solution and checked at 4 hour intervals and curves plotted similar to those in Fig. 9. The point where an appreciable break was noted in the electrical resistance-time curve was taken as the time when the intergranular bond began to waste away.

The methods prescribed in which the two special heat treatments were used prior to testing are not to be considered entirely from an acceleration standpoint. If the high nickel-chromium austenitic steels are to be welded, some portion of the material is held within the temperature range at 1200° F. while others are heated to temperatures high enough to initiate carbide diffusion. Also in heat treating, providing the temperatures are not carefully controlled, the very practice which is designed to dissolve carbides also enhances diffusion.

This phenomenon of carbide dissolution and diffusion is in no way connected with grain growth because similar results are obtained with the same material in the "as-cast" condition wherein grain growth does not proceed with any degree of rapidity comparable with rolled material. Naturally the grains of worked metal grow at a much greater rate than those of the cast alloys.

Methods of Combating Intercrystalline Attack

It is possible by a suitable increase in chromium or by substituting additional elements having a greater affinity for carbon than chromium has, to maintain a matrix which defies attack even after the carbides are precipitated. However, at elevated temperatures wide grain boundaries still persist indicating the mobility of the remaining carbides. It seems as if the carbides tend to change their composition at the same time the dissolving action appears to have taken place. Chromium may be restored but some carbide of apparently different composition evidently diffuses and collects at the boundaries. The exact mechanism of this change the authors are not prepared to explain, but intergranular attack is not arrested following heat treatment at elevated temperatures. Seemingly the scattered location of the carbides, which appear after precipitation at 1200° F. is not as detrimental as the concentration of these particles in boundaries following higher temperature exposures. In any event wide boundaries which seem to precede intergranular attack are removed by reducing the carbon to a low value.

It is true that low carbon alloys form sluggish mixtures which present serious problems in the production of sound sand castings. However, by the judicial use of residual silicon, the employment of mechanical methods of feeding, unknown in the average steel foundry practice and utilization of efficient and scientific deoxidation, it is possible to diminish the surface tension of these alloys and produce sound castings of a high quality.

For ease in machining, low carbon austenitic alloys are of distinct advantage in high speed production. The use of higher carbon mixtures in which heat treatment is intentionally avoided to eliminate the diffusion tendency, presents difficulties in the machine shop, although the evils of precipitated carbides may produce no deleterious effects from corrosive influences where higher chromium contents or more expensive carbide forming elements are employed. Furthermore, welding must be avoided since this operation would again aggravate the tendency toward diffusion.

Physical Properties

In Table V the necessity of subjecting high carbon (L-25) castings to the Strauss Treatment is clearly shown in order to develop the maximum physical properties in addition to relieving strains. As mentioned previously such treatment is detrimental when the intercrystalline type of corrosion is taken into consideration. With the low carbon material (L-4) the Strauss Heat Treatment is not essential for improved physical properties and in the event heat treatment for the removal of casting strains is deemed advisable, lower temperatures may be employed to a distinct advantage. Heating in a temperature range between 1700° and 1900° F. should prove ample to relieve strains, since it is not necessary to soak the castings at higher temperatures which might produce distortion or grain growth.

Table V. Average Physical Properties of "L" Grade Alloy

Alloy	Form	Heat Treatment	Ultimate Strength lbs./in.^{2}	Yield Point lbs./in.^{2}	% Elong in 2"	% Reduction of Area
L-25	1" Hot Rolled rod	Natural Condition	120,000	96,000	28.5	47.5
L-25	1" Hot Rolled	Annealed	104,850	34,000	44.5	47.5
L-25	Sand Castings	Natural Condition	45,000	26,000	7.5	12.5
L-25	Sand Castings	Annealed	62,250	27,000	32.5	32.5
L-4	1" Hot Rolled rod	Annealed	85,000	33,000	67.5	67.5
L-4	Sand Castings	Natural	67,900	28,750	45.7	45.5
L-4	Sand Castings	Annealed	68,500	29,750	50.7	45.6

Summary

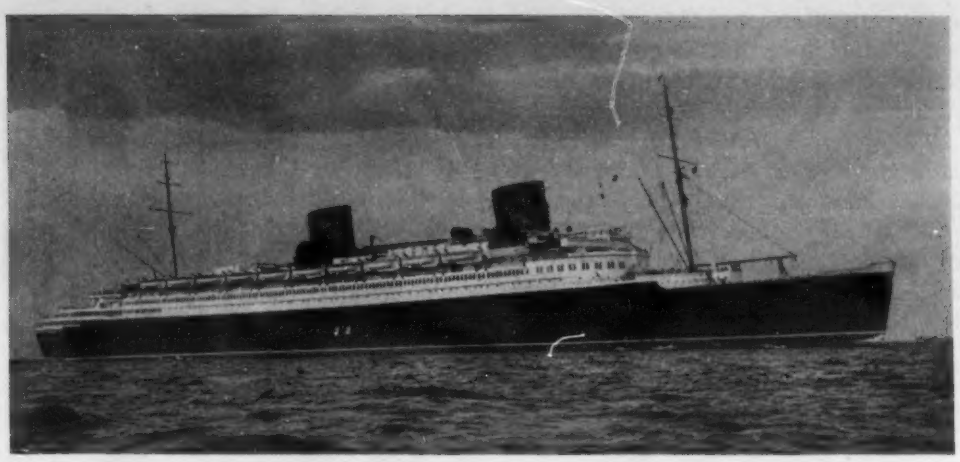
The technique of laboratory testing outlined has been developed from experience obtained in actual service trials. In many instances, failure due to accelerated tests conducted on samples intentionally heated at 1200° F. or temperatures exceeding 2150° F. are reported in less than 100 hours. Although the heat treatments represent extremes in some cases, the solutions are typical and these seemingly early failures are representative of actual plant tests which were run to destruction in periods ranging from two to eight months. In other words, the phenomena of diffusion described by soaking at 2250° F. yields results in the laboratory in a few hours whereas the same results are obtained in service with treatments at 2050° F. in a few months.

Air quenching was substituted for water quenching in the Strauss Treatment due to the fact that difficulties are encountered in treating tanks and other large objects by the latter method. Similarly intricate castings are subject to distortion because of the higher temperatures used and additional strains are set up following the more drastic quench.

The deleterious effects of high carbon are relieved when only carbide precipitation without regard to mobility of the particles is considered. This is accomplished by increasing the chromium or by the addition of other elements having a greater affinity for carbon than that shown by chromium. The high temperatures necessary for carbide solution still exert the same evil effects.

If heat treating is avoided for the reasons explained, welding likewise is prohibited and the desirable qualities of better mechanical properties, machinability and freedom from casting strains must also be sacrificed.

Steel pickling solutions have been employed to illustrate the mechanism of intergranular corrosion but other corrosives producing similar attack are governed by the same principles of carbide precipitation and dissolution.



S. S. Bremen

IZETT STEEL

What It Is and What It Is Used For

By G. G. NEUENDORFF

FAILURE of boilers, due to embrittlement resulting from corrosion, has led to the development in Germany of a specially-finished "Izett" steel claimed to be an improvement. No very general interest has developed in this steel in this country, perhaps because of the results obtained in tests by Parr and Straub. Dr. Neundorff raises a question whether these tests proved any inferiority of the German steel for boiler purposes. However that may be, it has peculiar and interesting properties which may bring it into use other than for boilers.

Izett steel is, so far, a Krupp proprietary product and even in this comprehensive review of its properties, there are given no details of the steel making procedure required. While other and more complex deoxidizing practice may perhaps be employed, it seems probable that the kink is the addition of aluminum to a heat at a rather definite stage of oxidation. Apparently indiscriminate killing of the steel with aluminum is not the whole story, and the deoxidation is probably more or less of a hair-trigger matter.

It seems likely that other methods of scavenging would produce similar results and that more than one finishing method might give an "always tough" steel. The fact that such a steel is produced, not merely as a freak melt, but with a regularity that apparently makes it a commercial product when one knows the trick, indicates that, in experienced hands, it is probably not so touchy as American steel makers are prone to believe.

One wishes that data were available as to ingot yield, propensity to surface defects and other economic factors that would allow appraisal of its probable cost when a tonnage demand develops. More information on weldability is also needed.

This general type of steel is very likely being given attention by a few American steel makers, but if so, they are keeping the results of any real experiments in its production under their hats.

As soon as such a steel is readily procurable, there are many uses beside boilers where brittleness caused by aging or produced by cold working (or both), is disadvantageous, for which it might well be tried. If the surface is satisfactory, it would be very interesting material to study in respect to some deep-drawing problems, on account of its extremely slow rate of hardening on cold-working.

WHEN the "Bremen" slipped into New York Harbor on her maiden trip, the papers described the features of the new Queen of the Seas. There was mention of a new Krupp steel which had been used for the boiler. It is called Izett steel from the German, "I(mmer) Z(äh)" meaning "always tough." Very little information has been published in the United States in regard to this steel.

This paper, in reviewing all that has become known in Germany on Izett steels, endeavors to summarize the principal facts.

In a paper before the "Vereinigung der Grosskesselbesitzer" on September 17, 1926 at Kassel dealing with the behavior of boiler materials in practice, Fry[1] raised the question, whether the boiler steels used at present actually meet all requirements. In every country, the maker of boiler steel must be particularly careful in making the steel, and the fabricator must choose his steel with care and test it thoroughly in order to avoid failures. Yet failures do occur.

The causes of these failures are manifold and must be strictly distinguished. Frequently they begin with the occurrence of fine cracks at the edge of rivet holes or at other places that have been worked while manufacturing the boiler. Under continued operation of the boiler, these cracks grow to such an extent that they may finally cause an explosion unless they are observed in time to avert disaster.

Investigations by Bauer[2] and many others showed that the development of such cracks is due to a preceding local cold deformation which is hard to avoid in processing a boiler. The brittleness which is brought about by this cold deformation develops gradually and attains its maximum only after some length of time, depending upon the temperature to which the material is subjected. The steel ages. The effect of aging upon the mechanical properties of steel has been studied. An illustration of the effect of aging upon the notch toughness is given in Table I.[3] Strips of a common boiler plate deformed by compressing by 2 mm., then made into notched impact specimens, $8 \times 10 \times 100$ mm., and tested with a 10 mkg. Charpy machine. It is shown that in aging at room temperature even one year is not sufficient to bring about the maximal aging effects.

Table 1. Results of Notch Impact Tests on Compressed Bars after Various Aging Times.

Deformed and tested	Notch toughness mkg./cm.²
Tested the same day	6.3
Aged 1 day at room temperature	4.7
Aged 7 days at room temperature	4.4
Aged 30 days at room temperature	4.3
Aged 90 days at room temperature	3.5
Aged 180 days at room temperature	3.3
Aged 360 days at room temperature	3.2
Aged 360 days at room temperature and then 2 hours at 250° C.	2.0

Interesting are also the investigations by Goerens[4] which illustrate the marked effect of aging upon the notch toughness of low carbon boiler steel but the slight effect upon nickel steels, as shown in Fig. 1. Whereas we see the notch toughness of C steel decreasing from 25 mkg./cm.^{2} to 2.8 mkg./cm.^{2} after cold working and a 10 days aging at 200° C., the notch toughness of the 3% Ni steel decreases only from 27.3 to 25.8 mkg./cm.^{2} and that of the 5% Ni steel only from 26.5 to 24.1 mkg./cm.^{2} Nickel steels are not only so much less sensitive to aging, but also have much better mechanical properties at elevated temperatures which makes them ideal boiler steels, except for the price.

The formation of cracks under the influence of the boiler feed water is closely related to the aging effects as investigations have shown.[5] Such failures can be traced to changes or chemical reactions of the water with the boiler material. There must also be mentioned here the embrittlement of iron and steel by hydrogen, and all precautions must be taken to avoid the development of nascent hydrogen in steam boilers. Not only does hydrogen directly embrittle the material but it aggravates the brittleness brought about by aging after cold deformation.

Local changes in the composition of the water can easily occur at even the slightest porosities along the joints of plates or underneath rivet heads. The water may then be enriched in alkaline substances and cause the well known caustic brittleness. There must, also, be considered the problem of electrolytic corrosion when local changes of concentration appear in the electrolyte present.

When the water contains higher amounts of alkaline substances, it is still more dangerous.[6] The destruction of aged steel is accelerated, the higher the concentration and the temperature of the alkaline water.[7] Though the opinions vary as to this point, it is generally assumed that the frequently observed intercrystalline fracture of boiler material is caused by alkaline substances which penetrate into the interior of the structure and eat up the substance between the grains. Such failures due to caustic brittleness have repeatedly been reported, to mention only the valuable investigations by Parr and Straub[6] or those by Pomp and Bardenheuer.[2]

Aged steels also corrode more rapidly. Warner[8] was successful in establishing a relation between the occurrence of Fry's strain figures and an increased tendency to local corrosion at places of severe cold work. In the special case of a vessel which had been used for storing mixed acid, i. e., a mixture of 90% HNO_3 and 10% H_2SO_4 (which is an excellent reagent to develop Fry's figures), the destruction was clearly shown in a cold bent ring. The end of this ring had been hot bent and had practically not been corroded. In accordance with these findings, Körber and Pomp,[2] in investigating some parts of steam boilers that had failed, reported on corrosion which had proceeded along lines at angles of 45°. A close relation between this characteristic corrosion and Fry's strain figures became evident.

All these facts go to show that a large percentage of boiler failures must be traced to the impairment of the properties of the steel used by aging effects.

What, then, are the remedies to avert aging and what, besides alloying, are the possibilities in improving boiler steels? Before Fry (well known for his invention of the nitriding process) developed the new non-aging steel, it was known that low carbon melts of normal production show a variable tendency for aging; sometimes they are practically free from aging and other times they show the phenomenon in a pronounced manner. This occurrence pointed the way to go about the problem for, if various heats of the same nominal chemical composition show a variable tendency toward aging, the metallurgy of the steel-making process, itself, must be the primary consideration.

Along this line, i. e., a metallurgical treatment of the steel bath, Fry developed the non-aging Izett steel. It is necessary to point out that the metallurgy of Izett steel does not pertain to alloying at all. Fry's method of making the steel can be applied to any type of steel in order to improve its qualities and it, therefore, is nothing other than a method of procedure.

From this point of view, it will be understood that there is practically no information available on the making of the steel. But we find a hint in the fact that carefully deoxidized

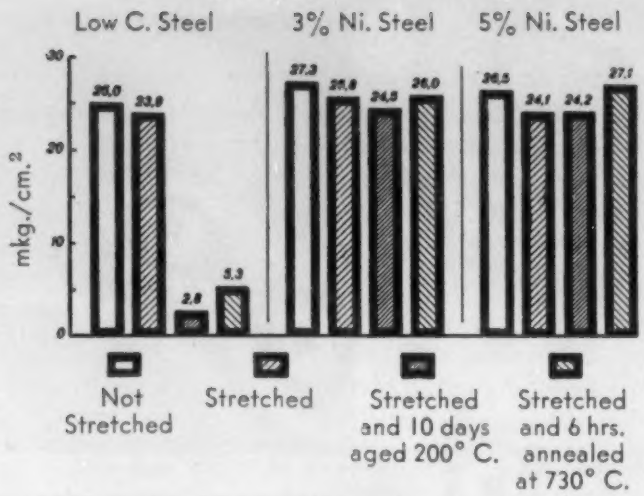


Fig. 1. Effect of Cold Work, Aging and Recrystallization upon Notch Toughness.

steels are known to show much less tendency for aging than semi-killed or rimmed steels. Thus, while making Izett steel, the steel bath is treated with strongly deoxidizing reagents. Izett steel is a carefully deoxidized steel. As will be later seen, the excellent properties can also be imparted by heat treating the rolled finished product. Another method of procedure is a combination of both of these methods.

Izett steel is delivered in 4 grades which do not differ in composition, save for the carbon content, to meet the requirements of the standards of the German Steam Boiler Association which prescribe:

Class I	tensile strength	50,000-62,500 lbs./in.^{2}
Class II	tensile strength	58,000-71,000 lbs./in.^{2}
Class III	tensile strength	62,500-75,500 lbs./in.^{2}
Class IV	tensile strength	67,000-79,500 lbs./in.^{2}

A typical analysis of Izett Class I steel is: C, 0.13; Si, 0.02; Mn, 0.58; P, 0.012; S, 0.015.

It certainly will be of interest to the practical metallurgist to know whether the particular melting and finishing procedure in making Izett steel needs great skill and offers difficulties. Though the inventor of the new steel once pointed out, himself, that the successful making of Izett steels depends somewhat upon the experience of the individual metallurgist in charge of the process, it becomes obvious from Fig. 2 that the experienced metallurgist can practically always obtain the best results. This diagram summarizes the results of notch impact tests on 60 heats of Izett steel which were made by the Krupp Works between May and June 1930. The notch toughnesses plotted are those of aged specimens and show that among these 60 heats there are only 8 with a notch toughness below 25 mkg./cm.^{2} Of the heats, 50% had a notch toughness between 25 and 30 mkg./cm.^{2}

In accordance with the results previously mentioned on the detrimental effect of cold work upon the mechanical properties and its simple detection by Fry's etching method, it may be mentioned that such strain figures cannot, by the normal procedure, be revealed in Izett steel.

The question whether the notched bar impact test does actually give proper evidence of the aging properties cannot be discussed here. It may be pointed out, however, that at certain temperatures every material has a transition range from high to low values of notch toughness and that this zone of decrease of notch toughness depends upon a great variety of conditions, as for instance structure, previous heat treatment or mechanical treatment, dimensions of the specimens, shape of the notch, velocity of the impact, etc. In testing the aging properties by means of the notched bar impact test, the testing conditions must always be considered and they must be comparable.

When the first results of investigations were published, it was astonishing to see that the new steel is far superior to common boiler steel. Fig. 4 is taken from an investigation of the material testing laboratory at the Technische Hochschule, Stuttgart, the results of which were presented by Baumann at a meeting of the "Allgemeiner Verband der Deutschen Dampfkesselüberwachungsvereine" at Zurich on September 7, 1926 and confirmed by Fry at the above mentioned meeting at

Fig. 2. (left) Notch Toughness in Aged State.

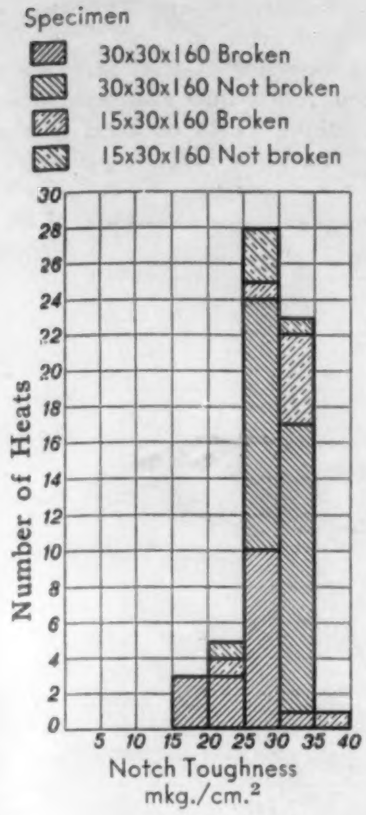
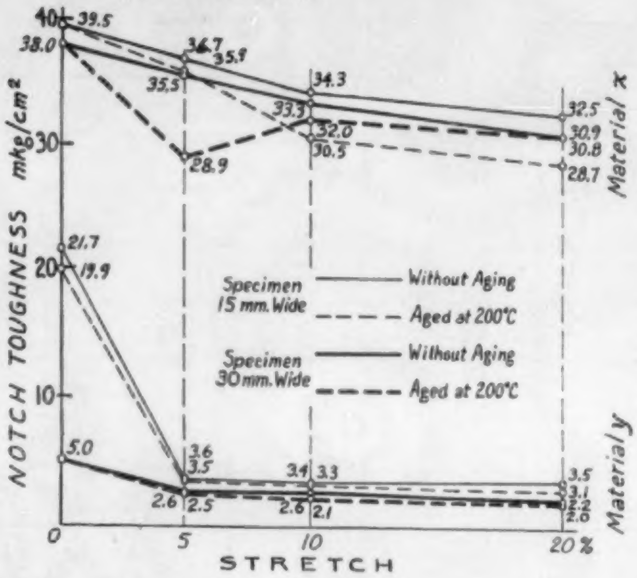


Fig. 3. Notch Toughness of Stretched Common Boiler Steel (y) and of Izett Steel (x) (R. Baumann.)



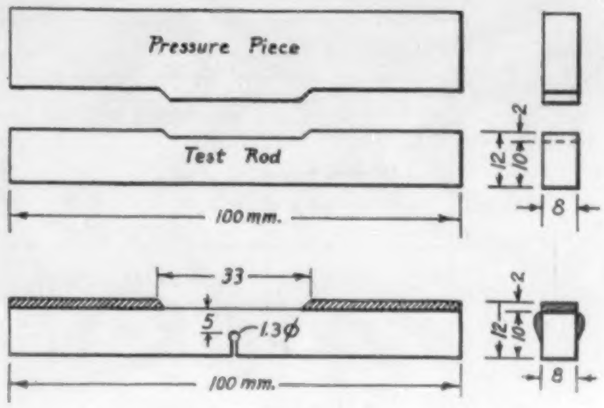


Fig. 4

Kassel. The curves of Fig. 3 were obtained on specimens of both common boiler steel and Izett steel 15 and 30 mm. wide, respectively. The materials had been stretched by 5, 10 and 20% and the notch toughness was either immediately determined or after an aging at 200° C. for 1/2 hour. This diagram shows that whereas the notch toughness of Izett steel decreases but slowly even after a stretching by 20% and subsequent aging, the common boiler steel shows a very marked decrease of notch toughness after stretching by only 5% and aging.

Other tests were performed on severely deformed, compressed specimens according to the method of Bauer.[9] This method is as follows: Strips 8 × 12 × 100 mm. are taken from the plate to be tested and compressed by 2 mm. in the middle of the bar on a length of about 33 mm. and then made into impact specimens of 8 × 10 × 100 mm. as shown in Fig. 4. A microscopic examination proved the material to be free from segregations and blowholes, showing a normal structure of ferrite with a few areas of pearlite, corresponding to a carbon content of 0.13%. The specimens had been subjected to the following treatment: The first group of specimens were taken from the plate in the rolling direction; compressed by 2 mm. as delivered; aged at various temperatures for 2 hours and tested. The second group of specimens were also taken in the rolling direction; annealed at 900° C. for ½ hour; cooled in the furnace; then compressed by 2 mm.; aged and tested. The third group is taken transverse to the rolling direction but otherwise treated as the second group. The results are given in Table 2. Table 3 gives some information on the notch toughness of the material as delivered and after 1/2 hour annealing at 900° C.

Table 2. Notch Toughness of Aged Izett Class I Steel

(For dimensions of specimens see Fig. 4)

After compressing aged 2 hrs. at °C.	1 Specimens in rolling direction, compressed as delivered, aged. Notch toughness mkg./cm.²	2 Specimens in rolling direction, annealed, compressed, aged. Notch toughness mkg./cm.²	3 Specimens transverse to rolling direction, but otherwise as 2. Notch toughness mkg./cm.²	Mean value of columns 1, 2 and 3
not aged	10.9	6.7	6.9	8.2
50	10.2	6.8	6.9	8.0
100	10.2	6.3	7.1	7.9
150	7.6	7.9	6.2	7.2
200	6.9	4.6	6.2	5.9
250	4.4	3.3	3.7	3.8
300	4.4	5.4	3.7	4.5
350	6.5	4.3	4.1	5.0
400	7.7	6.8	5.5	6.7
450	8.0	7.9	7.1	7.7
500	9.5	8.9	7.7	8.7
550	12.0	9.5	7.9	9.8
600	13.2	13.5	12.8	13.2
650	14.2	13.4	13.7	13.8
700	14.0	14.7	14.2	14.3
750	11.3	12.1	10.5	11.3
800	13.5	12.0	10.4	12.0
850	13.7	14.7	12.4	13.6
900	13.3	14.2	13.2	13.6

The above values are the mean values of 2 to 4 individual values.

Table 3. Notch Toughness of Izett Class I Steel

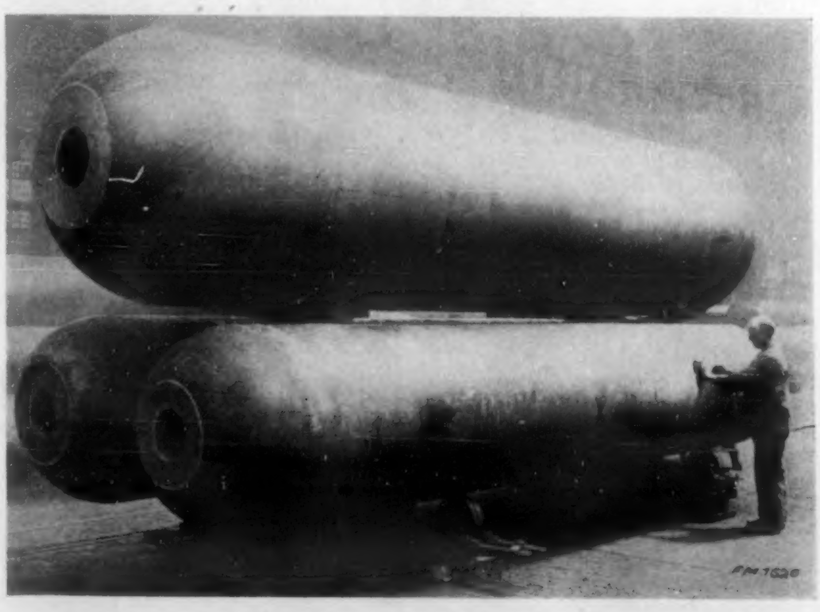
State of material and location of test bars in plate	Notch toughness mkg./cm.²
As delivered—rolling direction	14.6
As delivered—transverse to rolling direction	13.4
Annealed ½ hr. at 900° C. and cooled in furnace—rolling direction	15.2
Annealed ½ hr. at 900° C. and cooled in furnace—transverse to rolling direction	12.7

The values are the mean values of 2 to 4 individual values.

The results are diagrammatically shown in Fig. 5 and are as follows:

1. The specimens compressed as delivered and then aged practically all show a higher notch toughness than those which have been annealed before compressing. The difference is largest with the specimens aged up to 100° C. Above an aging temperature of 150° C., the differences are less pronounced.

2. The effects of aging appear with increasing aging temperature. A minimum of notch toughness is attained at between 250° and 300° C.; the values range from 3.3 to 4.4 mkg./cm.² Comparative tests on 3 common boiler steels (C: 0.02, 0.07 and



Seamless High-pressure Drums of Izett II Steel.

0.28%) which had been subjected to the same procedure showed minima of notch toughness between 0.8 and 1.4 mkg./cm.[2] Table 4 gives the results obtained on the 0.07 C steel (designated A2U) and in Fig. 6 the results on A2U and Izett Class I are plotted together to facilitate a comparison. A comparison shows that, whereas the notch toughness of A2U

tures as they are found in high pressure boilers. This curing of the aging effects will be discussed later.

Further determinations of the properties of Izett steel were made on material which had been rolled into seamless tubes according to the Mannesmann method. Tests on steel of the same heat were carried on by the "Staatliche Materialprüfungs-

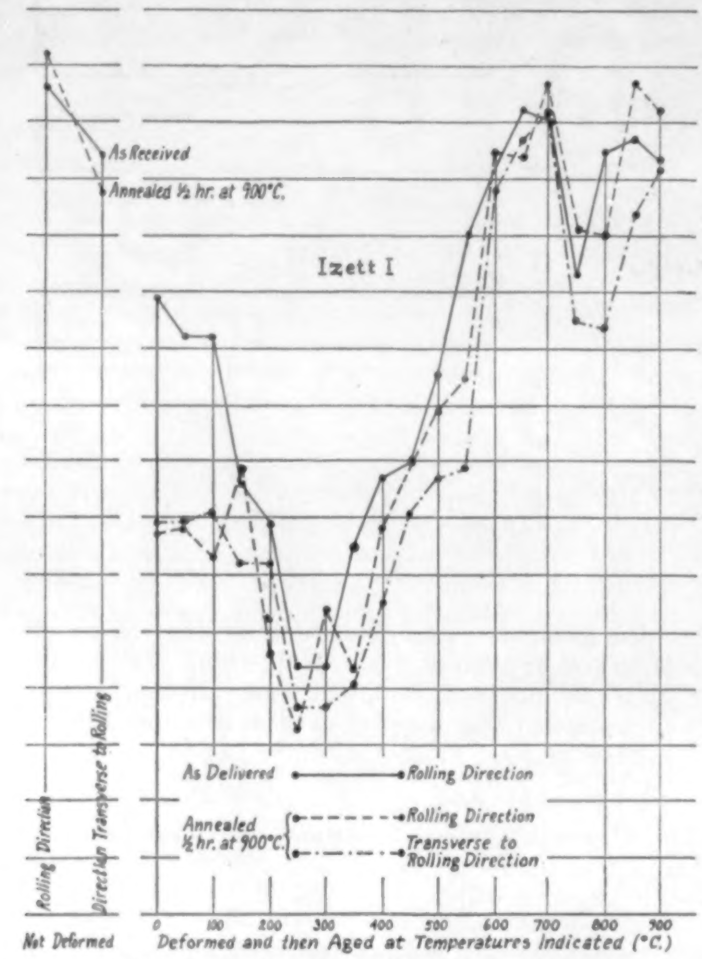


Fig. 5. Notch Toughness of Izett I.

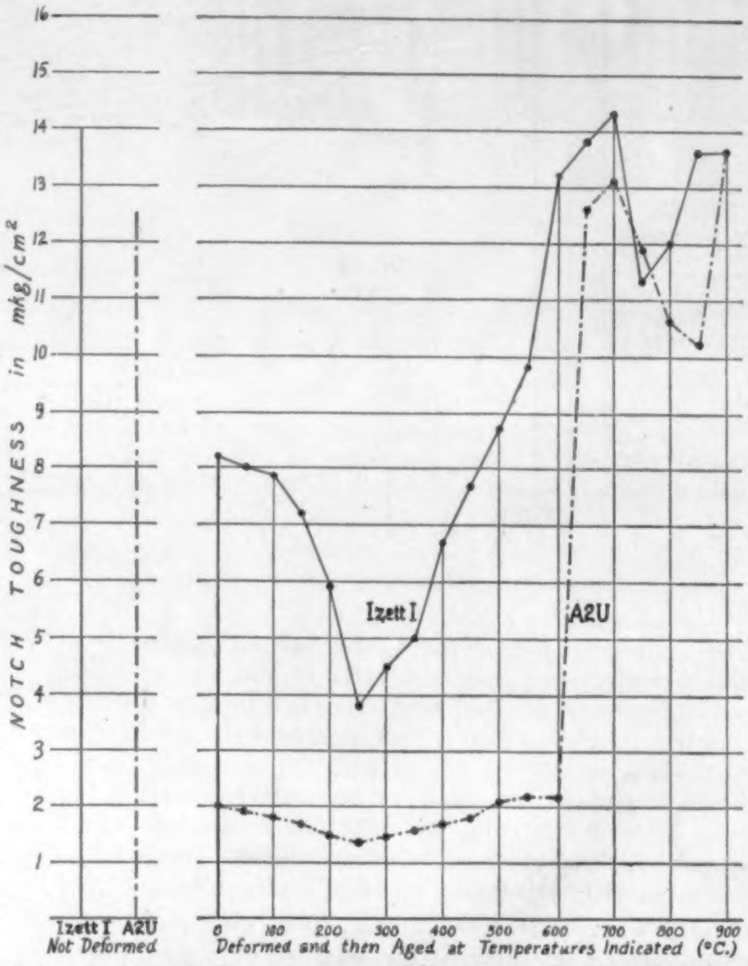


Fig. 6. Notch Toughness of Common Boiler Steel and Izett Steel.

does not increase below 600° C., the notch toughness of Izett steel decidedly increases again at an aging temperature of 350° C. In both cases, the maximal values are attained at temperatures of 650° to 700° C. The later repeated decrease of notch toughness at 750° to 800° C. for Izett Class I and 850° for A2U has nothing to do with aging effects. These are occurrences of grain growth due to recrystallization.

The results indicated that Izett steel when subjected to severe deformation is not entirely insensitive to aging effects, as was indicated by the first investigations which subjected the material to less severe deformations. However, the decrease of notch toughness is not nearly so pronounced and not extended over such a wide temperature range as with common boiler steels. The advantage of Izett steel is that its notch toughness again increases during aging at tempera-

Table 4. Notch Toughness of Common Boiler Steel with 0.07% C.

(Specimens annealed at 900° C. for ½ hr. before compressing)

Specimens in rolling direction. Notch toughness mkg./cm.² (mean value of 2 to 4 determinations)	After compressing aged for 2 hrs. at ° C. not aged	Specimens transverse to rolling direction. Notch toughness mkg./cm.² (mean value of 2 to 4 determinations)
2.0		2.0
1.7	50	2.1
1.8	100	1.8
1.7	150	1.6
1.5	200	1.5
1.4	250	1.4
1.5	300	1.5
1.6	350	1.5
1.8	400	1.6
1.9	450	1.7
2.0	500	2.1
2.1	550	2.2
2.2	600	2.2
13.0	650	12.1
13.5	700	12.6
12.5	750	11.3
11.0	800	10.1
10.5	850	9.8
13.7	900	13.4

amt," Berlin-Dahlem[10] and by the Mannesmann Tube Works at Düsseldorf-Rath. Since the results are practically the same in both cases, there need be given here only the more detailed results of the "Staatliche Materialprüfungsamt." The heat under consideration, containing 0.12% C, 0.03% Si, 0.45% Mn, 0.03% P, 0.003% S, had been rolled into tubes with an outside diameter of 96 mm. and a wall thickness of 3.5 and 7 mm., respectively.

The investigation comprised the following tests:

1. Macroscopic and microscopic examination.
2. Determination of the tensile properties at room temperature.
3. Determination of the notch toughness of specimens (a) as delivered, (b) annealed at 870° C., (c) annealed at 870° C., then stretched by 10, 15 and 20% and aged at 200° C. for ½ hour, (d) annealed at 870° C., then compressed by 2 mm. and aged for ½ hour at 200° C.
4. Technological tests, expanding tests, expanding tests with a mandrel having a slope 1 : 7, and cupping tests.

The results are as follows:

1. The macroscopic examination of neither of the tubes showed peculiarities. The microscopic examination of the thick-walled tube showed some more non-metallic inclusions than the thin-walled; but both of them had a normal structure of ferrite with small areas of pearlite.
2. The results of the tensile tests are given in Table 5.

As to the tensile strength, it is remarkable that Izett steel does not show an increase between 200° and 300° C., as does common low carbon steel. The tensile strength of 58,500 lbs./in.² at room temperature decreases but slightly up to 300° C., and then more at higher temperatures, giving a tensile strength of 50,300 lbs./in.² at 400° C. and of 34,800 lbs./in.² at 500° C.

3. The results on notch toughness are tabulated in Table 6. The values of the 3.5 mm. tube are the mean values of 5 determinations; those of the 7 mm. tube, the mean values of 3 determinations.

The slight decrease of notch toughness of the stretched and even of the compressed and then aged specimens illustrates the high stability of Izett steel against aging.

4. The normally prescribed requirements of low carbon steels for the above tests were met by both tubes. They could be widened and cupped to the prescribed extent without showing any cracks.

Another comprehensive investigation of Izett boiler plates of various carbon content was carried on by the material testing laboratory of the Technische Hochschule, Stuttgart. The results were present by Ulrich[11] at the Annual meeting of the "Vereinigung der Grosskesselbesitzer" on September 7, 1927 at Düsseldorf. In these tests, there were determined the tensile properties and the notch toughness at 20°, 200°, 300° and 450° C. of specimens as delivered and of specimens that had been deformed and aged at 250° C. for ½ hour, 2, 100 and 200 hours. The 4 classes of Izett plates delivered met the previously mentioned requirements. For every type of test, 6 specimens were tested, taken from both ends and the middle

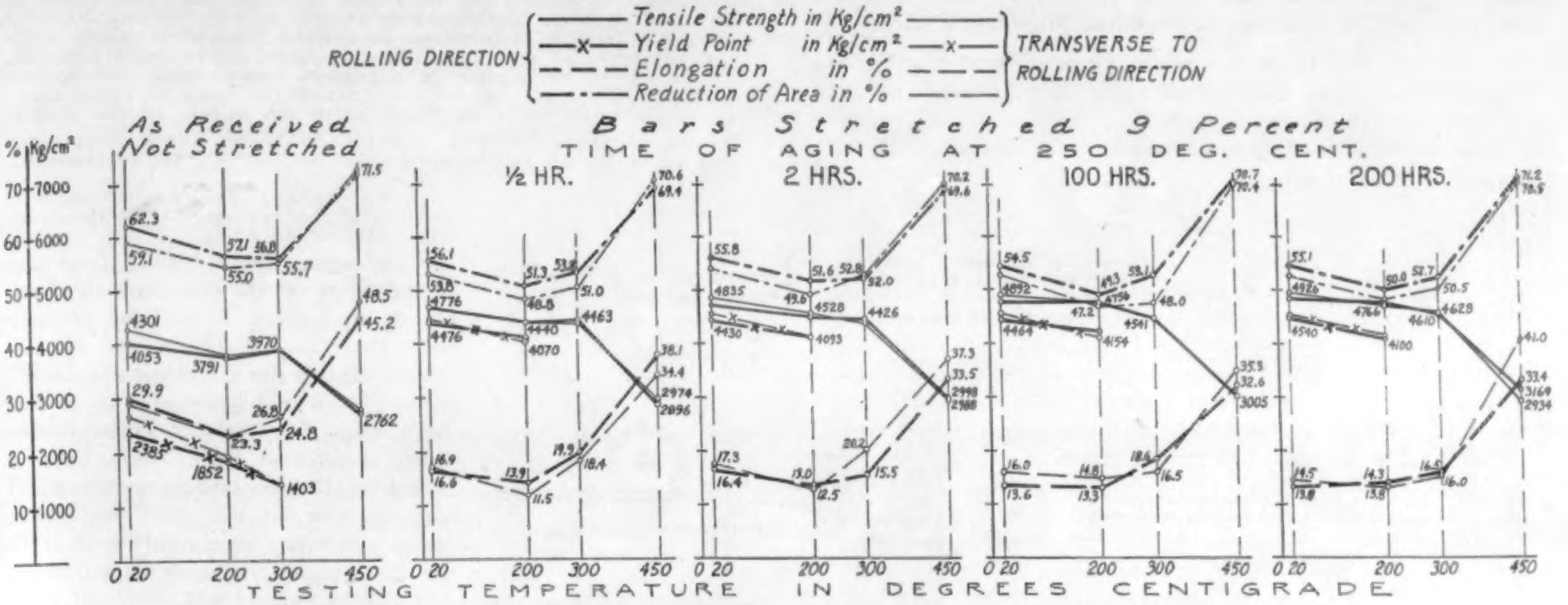


Fig 7. Results of Tensile Tests on Izett II in Dependence upon Temperature.

Table 5. Mechanical Properties of Izett Steel at Various Temperatures

Testing temperature ° C.	Yield point lbs./in.²	Tensile strength lbs./in.²	Elongation %	Reduction of area %
20	44,000	58,500	30.0	61.5
200	35,200	56,100	21.8	60.0
300	24,400	55,500	24.0	57.0
400	22,000	50,300	39.1	70.0
500	18,200	34,800	46.7	67.0

Mean values of 5 tests at each temperature

Table 6. Notch Toughness of Izett Tubes after Varying Treatments.

Treatment	Notch toughness mkg./cm.² 3.5 mm. tube	Notch toughness mkg./cm.² 7 mm. tube
As delivered	13.2	12.7
Annealed at 870° C., 1 hr. air cooled	14.3	15.8
Annealed at 870° C., 1 hr. air cooled, stretched by 10%, aged at 200° C. ½ hr.	12.0	12.9
Same as above but stretched by 15%	11.8	11.8
Same as above but stretched by 20%	12.4	11.5
Annealed at 870° C., 1 hr. air cooled, compressed by 2 mm., aged at 200° C. ½ hr.	11.7	11.3

of the plates, in the rolling direction as well as transverse to the rolling direction. In order to bring about the deformation, strips of plates were stretched in a tensile testing machine as follows: Izett I by 10%, Izett II by 9%, Izett III by 8%, Izett IV by 7%.

The following results and discussion refer to the tests on the Izett II plate. Table 7 and Fig. 7 show tensile strength, yield point, elongation and reduction of area of the plate as delivered and after stretching by 9% and aging at 250° C. for ½ hour, 2, 100 and 200 hours. Table 7 has been compiled from the figures written down on the curves. Since some of the values are missing, they have been given by interpolation. The figures have not been converted from kg./cm.² into lbs./in.² to avoid confusion in comparison with the figures of the diagrams.

As to the properties in the state as delivered, it is evident that again, as in the previous investigation, there is absent the maximum of tensile strength around 250° C. The values of tensile strength obtained at room temperature, 200° and 300° C. show no large deviation, the one from the other. The elongation decreases from 29.9% at room temperature to 23.3% at 200° C., thus showing at this temperature an essentially higher value than common boiler steel II, which at this tem-

Table 7. Mechanical Properties of Izett II Plate, as Delivered and after Stretching and Aging at 250° C. for ½ hr., 2, 100 and 200 hrs.

Treatment of specimen	Testing temperature ° C.	Tensile strength kg./cm.²		Yield Point kg./cm.²		Elongation %		Reduction of Area %	
		Rolling direction	Transverse	Rolling direction	Transverse	Rolling direction	Transverse	Rolling direction	Transverse
As delivered	20	4053	4301	2385	2694	29.9	29.0*	62.3	59.1
Aged ½ hr.	20	4776	4776	4476	4500*	16.6	16.9	56.1	53.8
Aged 2 hrs.	20	4700*	4835	4430	4550*	16.4	17.3	55.8	53.7
Aged 100 hrs.	20	4750*	4892	4464	4550*	13.6	16.0	54.5	53.0*
Aged 200 hrs.	20	4900*	4926	4540	4570*	13.9	14.5	55.1	53.2
As delivered	200	3791	3800*	1852	1900*	23.3	23.3	57.1	55.0
Aged ½ hr.	200	4449	4440	4105	4070	13.9	11.5	51.3	48.8
Aged 2 hrs.	200	4500*	4528	4093	4120	13.0	12.5	51.6	49.0
Aged 100 hrs.	200	4756	4785	4233	4154	13.3	14.8	49.3	47.2
Aged 200 hrs.	200	4800*	4766	4100	4148	14.3	13.8	50.0	48.6
As delivered	300	3970	3970	1403	——	24.8	26.8	56.8	55.7
Aged ½ hr.	300	4463	4417	——	——	19.9	18.4	53.8	51.0
Aged 2 hrs.	300	4426	4382	——	——	15.5	20.2	52.0	52.8
Aged 100 hrs.	300	4511	4541	——	——	18.6	16.5	53.1	48.0
Aged 200 hrs.	300	4610	4628	——	——	16.5	16.0	52.7	50.7
As delivered	450	2762	2800*	——	——	45.2	48.5	71.5	72.3
Aged ½ hr.	450	2896	2974	——	——	38.1	34.4	69.4	70.6
Aged 2 hrs.	450	2998	2958	——	——	33.5	37.3	69.6	70.2
Aged 100 hrs.	450	3005	3100*	——	——	32.6	35.3	70.7	70.4
Aged 200 hrs.	450	3169	2934	——		33.4	41.0	71.2	70.5

*Approximate

perature has an elongation of about 16%. At room temperature an elongation of 20-24% is prescribed for class II. The increase of tensile strength by stretching and subsequent aging is clearly shown in Fig. 7. The increase is very noticeable at the testing temperatures of 20°, 200° and 300° C., but not at 450° C. The elongation of the stretched and then aged specimens up to the testing temperature of 300° C. is naturally essentially lower than that of the specimens which have not been stretched. The differences are less pronounced at 450° C.

In plotting in Fig. 8 the above properties at the various temperatures against the time of aging, the difference between stretched-aged and non-stretched specimens again becomes obvious, as well as a slower increase of tensile strength with proceeding time of aging.

Fig. 9 shows the notch toughness plotted against the testing temperature in individual diagrams for various times of aging. The conclusions to be reached are as follows:

1. The notch toughness of the specimens as delivered with the width of specimen equal to the thickness of the plate is 16.7 mkg./cm.[2] in the rolling direction and 15.2 mkg./cm.[2] transverse to the rolling direction. The corresponding values for the specimens 15 mm. wide are: 21.3 mkg./cm.[2] and 18.3 mkg./cm.[2], respectively. In comparing the diagrams 9a and 9b, there is shown the decrease of notch toughness due to aging and it is, furthermore, shown in Fig. 9c and Fig. 9d that the notch toughness decreases somewhat more with longer times of aging, but the greatest decrease is brought about by ½ hr. aging. The lowest mean value which has been obtained is that of the transverse bars at room temperature with 9.0 mkg./cm.[2] after an aging of 100 hours.

2. All diagrams of Fig. 9 show that the notch toughness increases in all cases up to 200° to 300° C., to decrease at 450° C.

3. The values of the specimens in rolling direction are above those of the transverse ones.

Considering these results from the standpoint of the German designer of steam boilers, it may be pointed out that the specifications of the "Vereinigung der Grosskesselbesitzer" prescribe a notch toughness of 8.0 mkg./cm.[2] for Class II boiler plates with transverse bars which have a width of 15 mm. and have been aged for ½ hour at 200° C. The lowest value which has been found with Izett II steel under the above conditions, but for an aging temperature of 250° C., amounted to 12.4 mkg./cm.[2] with an aging temperature of 200° C., this value would be somewhat higher.

The results of the tests on Izett steels I, III and IV cannot be discussed in detail because of the many data which, of necessity, had to be dealt with. It will, however, be emphasized that the Izett steels of all the 4 classes meet the German specifications, as shown by the following table:

Class	Notch toughness aged Izett steel	Specified by German Steam Boiler Association
I	23.4 mkg./cm.[2]	8.0 mkg./cm.[2]
II	12.4 mkg./cm.[2]	8.0 mkg./cm.[2]
III	9.4 mkg./cm.[2]	7.0 mkg./cm.[2]
IV	7.7 mkg./cm.[2]	not specified

In the discussion following the presentation of this paper, Fry made some interesting, valuable contributions on the processing of Izett steel, its properties and applications.[12]

As previously mentioned, Izett steel is generally subjected to a heat treatment before being used. Izett steel should be normalized at temperatures close above Ac_3. This steel offers

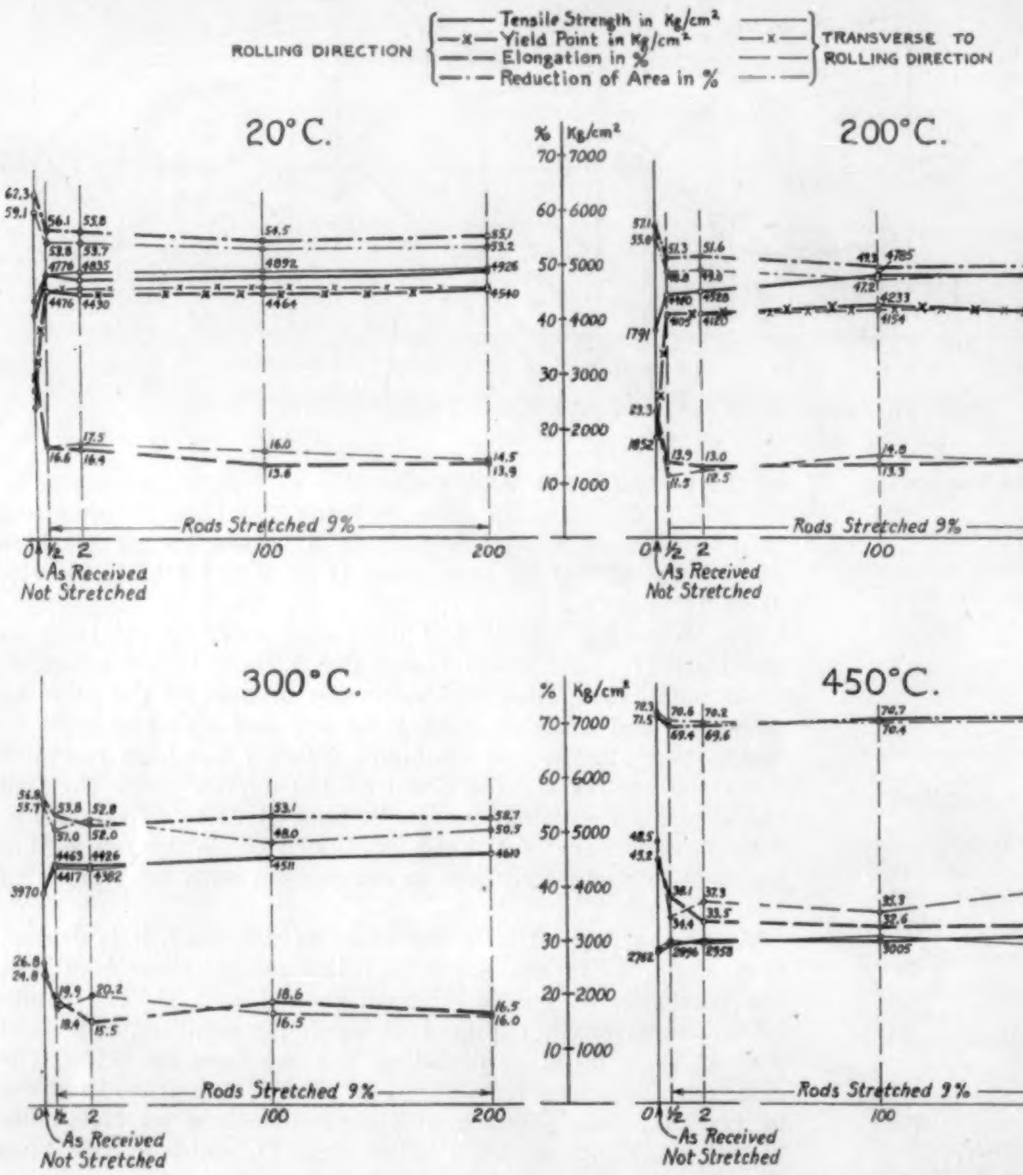


Fig. 8. Tensile Tests on Izett II at 20°, 200°, 300° and 450° C.

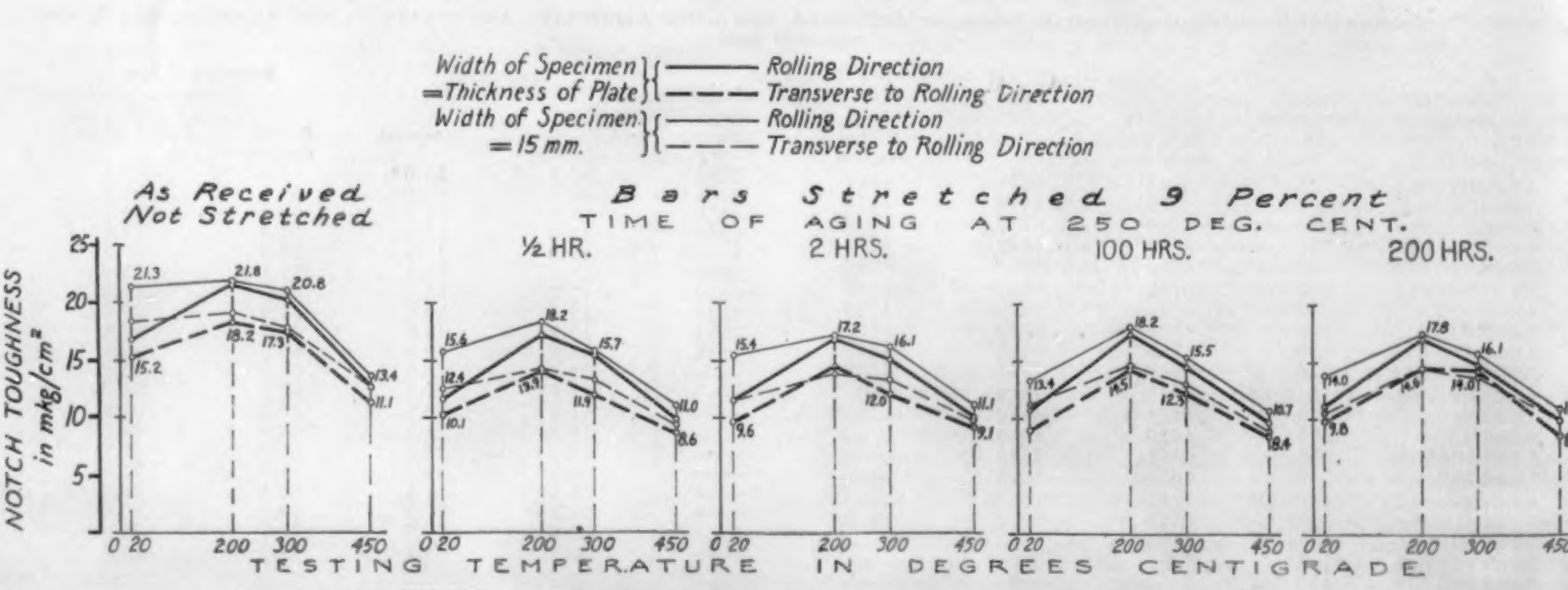


Fig. 9. Notch Toughness of Izett II in Dependence upon Temperature.

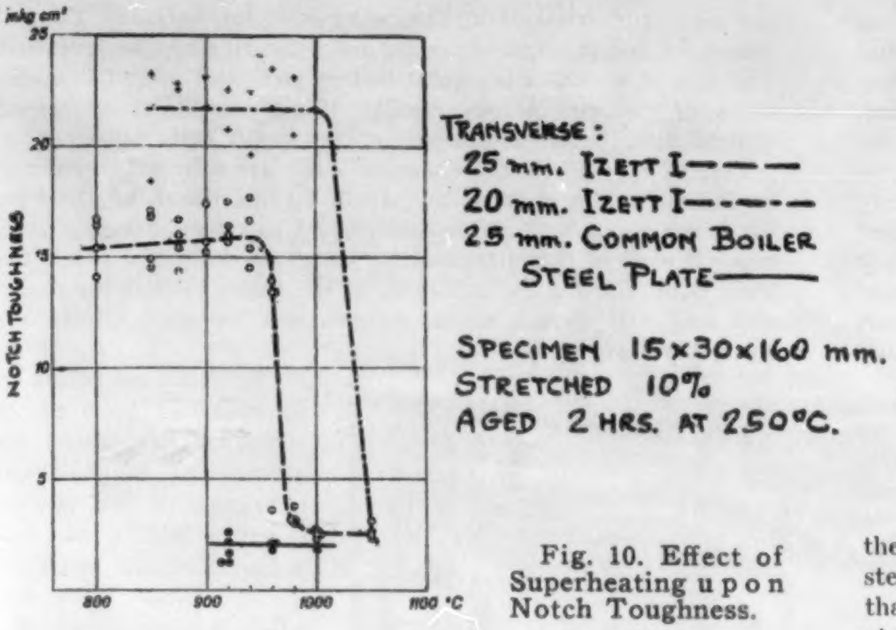


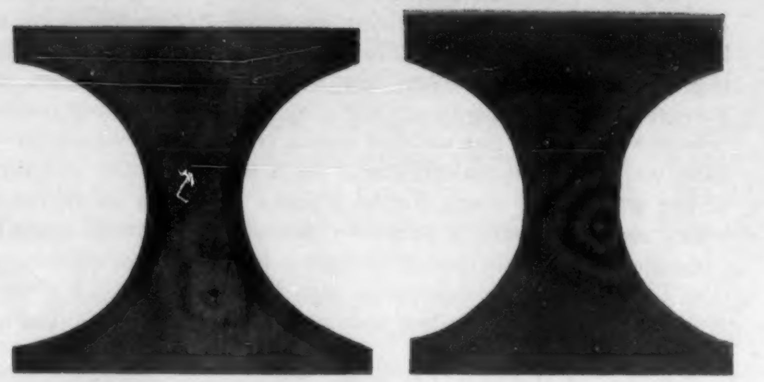
Fig. 10. Effect of Superheating upon Notch Toughness.

another advantage, as it is not so sensitive towards superheating as common boiler steel. Superheating, however, is disadvantageous, inasmuch as a subsequent aging essentially decreases the notch toughness. The effects of superheating can be remedied by regenerating the structure, i.e., normalizing above Ac_3. Table 8 and Fig. 10 illustrate these conditions.

By calling attention again to Fig. 7, there becomes obvious a peculiar tendency in Izett steel for the aging effects, which endanger the steel while in operation, to be cured. Aged Izett steel with a somewhat decreased notched toughness gradually regains its high notch toughness in time. This proves of high value in high pressure boilers which have to stand temperatures of 300° C. and above. The properties of aged Izett steel are not impaired but improved by continued operation at these high temperatures. This is substantiated by Table 9.

As to resistance to corrosion and caustic brittleness, Fry points out that the resistance to corrosion is about of the same order of magnitude as that of common boiler steel. Izett steels, however, are not so readily attacked by diluted sulphuric acid and show brittleness on account of pickling to a smaller extent than common boiler steels. Some information on this point is given in Table 10.

As to caustic brittleness, Izett steels are by far superior to common boiler steels, as has been substantiated by tests which have been carried out on a large scale by the Krupp Works and a large German chemical company. This does not become evident in the tests by Parr and Straub[6] who included Izett steel among the many steels which they investigated. For reasons unknown to the reviewer, flange steel and Izett steel (in



Common Boiler Steel I. Izett I.
Fig. 11. Strain Figures in Boiler Sections.

the above mentioned investigation designated "Special German steel plate") have been tested under various conditions, but so that the flange steel was subjected to a smaller load than Izett steel. While, in the one case, flange steel stood up better in the solution of NaOH, the reason appears to be the smaller load applied in comparison with the test on Izett steel. In the opinion of the reviewer, Parr and Straub tested Izett steel under conditions which do not permit arriving at conclusions of practical value. The publication which refers to the caustic embrittlement of Izett steel is an investigation by Ulrich[13] of the material testing laboratory of the Technische Hochschule, Stuttgart. The important results are given in Table 11. Attention may be called to the fact that, although Izett steel was subjected to a higher load (see ratio, test load to tensile strength), Izett steel stood up much better than flange steel, namely: in one case more than 13 times longer, and in the other case 2 times longer. After this result, the tests were discontinued, although the Izett bars were not yet broken.

Table 8. Notch Toughness of Izett I Plate after Normalizing, Super-heating and Regenerating.
Thickness of Plate: 25 mm.
Dimensions of Specimen: 15 × 30 × 160 mm., Round Notch, Diameter 4 mm.

Heat Treatment	Notch toughness mkg./cm.² Mean Values
Normalized	24.8
Normalized, then stretched by 10% and aged at 250° C. for 2 hrs.	16.1
Superheated at 1050° C. for ½ hr., not stretched	17.9
Superheated at 1050° C. for ½ hr., then stretched by 10%, and aged at 250° C. for 2 hrs.	2.6
Superheated at 1050° C. for ½ hr., then regenerated at 860° C. for ½ hr., not stretched.	24.6
Superheated at 1050° C. for ½ hr., then regenerated at 860° C. for ½ hr., then stretched by 10% and aged at 250° C. for 2 hrs.	15.4

Table 9. Effect of Aging Time upon the Notch Toughness of Izett I Steel

Heat Treatment	Notch Toughness mkg./cm.²
As delivered	21.5
Stretched 10%, aged at 500° C. for 300 hrs.	17.6
Stretched 10%, aged at 500° C. for 100 hrs.	17.2
Stretched 10%, aged at 300° C. for 300 hrs.	14.8
Stretched 10%, aged at 300° C. for 100 hrs.	11.8
Stretched 10%, aged at 300° C. for ½ hr.	9.4
Stretched 10%, aged at 200° C. for ½ hr.	9.8
Stretched 10%, aged at 250° C. for 2 hrs.	10.4
Stretched 10%, not aged	14.5

Type of Specimen: 25 × 30 × 106 mm., tested with 150 mkg. Charpy machine.

Table 10. Number of Bends and Loss of Weight of Izett Class I Sheets, 1.5 mm. Thick, Not Pickled and Pickled in H_2SO_4 (1:40) for 100 Hrs.

Legend:
I=Izett Class I
C=Common boiler steel
h=Annealed at high temperature (½ hr., 930° C., air-cooled)
l=Annealed low temperature (½ hr., 730° C., air cooled)
s=Stretched by 5%, not aged
Sa=Stretched by 5% and aged at 200° C. for ½ hr.

Symbol	Number of bends not pickled	Number of bends pickled	Loss of weight by pickling in grams
I h	21	14	0.61
I h s	20	16	—
I h Sa	17.6	14.2	1.31
I l	25	21	—
I l s	22	18	—
I l Sa	22.8	18.2	—
C h	21	9.5	1.37
C h s	18	7.5	—
C h Sa	16.5	6.8	2.37
C l	23	9.7	—
C l s	22	8.2	—
C l Sa	18	6.5	—

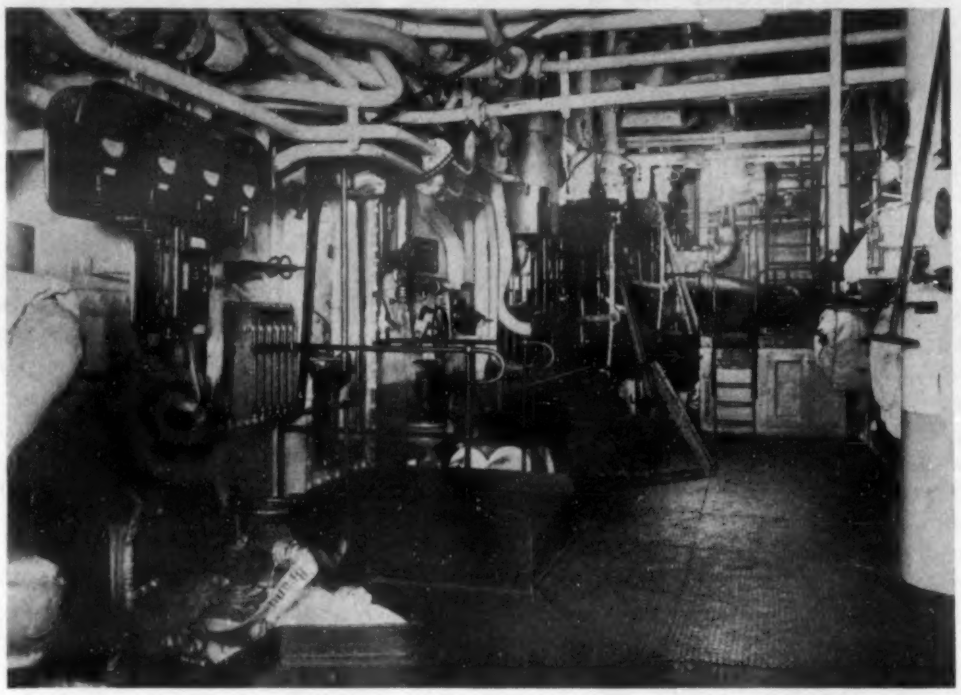
Table 11. Comparative Test on Caustic Embrittlement of Izett Steel and Flange Steel.
(Concentration of NaOH: 270-290 grams/liter)

Condition of Surface of test bar	IZETT-STEEL Ratio of test load to tensile strength at 20° C.	IZETT-STEEL Ratio at 250° C.	IZETT-STEEL Time of load days	IZETT-STEEL Result	IZETT-STEEL Elongation	FLANGE-STEEL Ratio of test load to tensile strength at 20° C.	FLANGE-STEEL Ratio at 250° C.	FLANGE-STEEL Time of load days	FLANGE-STEEL Result	FLANGE-STEEL Elongation
Planed, ground, with punch marks	0.82	0.88	20	not broken	7.5	0.80	0.68	1½	broken	4.2
Planed, ground, without punch marks	0.85	0.92	56	not broken	10.5	0.83	0.71	28	broken	9.5
Polished, without punch marks	0.90	0.97	52*	locally contracted	20	0.78	0.66	69½	broken	6.5

*The actual time cannot be given because of disturbances during the test.

Some few remarks may be made as to joining of Izett steel. Izett steel offers no difficulties in welding regardless of what kind of welding is used. It is noticeable that in fusion welding the weld seam no longer has the properties of Izett steel. Favorable results as to stability against aging have been obtained with water gas welded seams though the reason for this have not yet been ascertained. In a paper on the metallurgy of the welding of steel, Fry[14] states: "There is no doubt that boiler materials which are safe against aging can essentially promote the application of welding in steam boiler construction." And he, furthermore, says in concluding his paper: "Further progress in using welding in boiler construction must be based on a clear knowledge of the metallurgical problems and on the properties of the material. We are at the beginning of an important development."

As to riveting, a report has been published by Ulrich.[15] Various types of riveted joints of Izett Class I steel plates with a thickness of 35 mm. were tested with the result that the cold work around the rivet holes which had been brought about by riveting extended but to a small depth so that the notch toughness was not affected by aging. All these tests give evidence of the superiority of Izett steel.



View in Boiler Room of North German Lloyd S. S. Bremen.

In recent years, Izett steels have increasingly and successfully found application in Germany in the construction of various types of steam boilers, drums, chemical process vessels and many other purposes where it is necessary to use a material which shows no tendency toward aging or at least not to a dangerous extent. On page 63 are shown high pressure boiler drums for use at a pressure of 500 lbs./in.^{2}, installed at the new Krupp blast furnace plant at Essen-Borbeck. Boilers and tubes are made of Izett steel. Whenever Izett steel has been used for boiler construction, it was found that its working according to the methods common in boiler construction offers no difficulties. Difficulties which appeared in some cases could be traced to the fabrication of the finished product, but never to the steel itself. Some cases which have been reported by Fry may be discussed in order to dissipate any doubt as to the suitability of the new material.

In one case an order of Izett steel plates was rejected because of the material developing cracks while being pressed into bottoms of vessels. A metallographic investigation of the cracks showed occurrences of superheating and, in part, an excessive content of sulphur. The plates had been heated in coke fires. There were also indications that the pressing of the bottoms had not been performed with due precaution. The Krupp Works then used materials of the same heat for pressing some bottoms with dimensions like those which had failed. It turned out that the bottom could be pressed without the slightest indication of cracks and it was thus proven that the formation of the cracks was not due to the material but to a faulty pressing operation.

In another case, a company ordered Izett Class III steel and Izett Class I steel for a high pressure steam boiler to be used for the sectional chambers and the tubes, respectively. Preliminary tests on the adhesion in rolling-in the tubes into the chambers indicated the material to be unsatisfactory and it was assumed that Izett steel does not strain harden sufficiently during the rolling-in to give the tubes a tight fit in the chambers. In order to examine into this difficulty, comprehensive tests were carried on by the Krupp Works in coöperation with the company constructing the boiler and the customer. The adhesion of the tubes was tested not only at room temperature but also at elevated temperatures of 260° and 350° C. On the basis of the satisfactory results, the 3 companies concerned agreed that there were no objections to the material.

Fig. 11 shows how the chamber walls are affected in rolling-in the tubes. In etching for strain figures according to Fry, the black zones and stripes developed in common boiler steel make it evident that the material had been deformed above the yield point during the rolling-in of the tubes so that the material may fail during actual application. No such effects are shown by Izett steel.

The last case refers to an order of Izett plates which was rejected on account of the bad appearance of its fibrous fracture and it was assumed that the material would show porosity when subjected to deformations during the rolling-in of tubes. Tests showed that this assumption is unjustified; it could be substantiated that a fibrous structure appearing in tough plates neither endangers the rolled-in parts nor hinders the heat transfer.

If this review will help to arouse more interest in this steel among American metallurgists, the writer will feel that he has performed a useful service.

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Cadmium Plating vs. Corrosion-fatigue

Pickling vs. Corrosion-fatigue

By WILBER E. HARVEY*

The practical importance of protection against corrosion-fatigue by metallic coatings has been brought out by Haigh.† The tow ropes of the "Paravanes" used to protect shipping against mines during the war, failed due to combined vibration and corrosion. Galvanizing raised the life three or four times.

The protection afforded by a galvanized or plated zinc or cadmium coating is of course only temporary, so the "percentage protection" referred to in this article would hold only for a limited period. But even temporary protection is often very much worth while.

†B. P. Haigh. Chemical Action in Relation to Fatigue of Metals. Transactions Institution of Chemical Engineers, Vol. 7, 1929, pages 29-48.

INTRODUCTION

METAL FATIGUE is a phenomenon which has existed since metals have been used in dynamic parts. The use of metals for moving parts marked the advent of peculiarly early failures of parts whose design and construction warranted their safety for continued use. These premature failures remained permanent mysteries to engineers until the latter part of the nineteenth century. About 60 years ago, Wöhler, a German engineer and scientist, completed a study of metals subjected to repetition and alternation of stresses. Wöhler's results revealed that a material subjected to alternating stresses could not be expected to live an indefinite life if stressed to a value more than 40 to 50% of its static tensile strength. The fruition of these results was the development of better machinery. Following the tragic war of 1914 with its many fatal airplane accidents, a great many of which were due to a premature failure of some power plant part, the problem of fatigue was extensively studied by many able engineers. Problems of speed of machinery, design of parts and other variables in the study were completely analyzed by students of such fields with the result that now there are available many abstracts of works upon not only alternating flexure tests but also alternating longitudinal tension and compression tests, alternating bend and torsion tests and repeated impact tests. Designing has improved in such a rapid fashion that it is only necessary to study fatality results of commercial airway companies to realize the safety of the modern air travel service. The problem of fatigue seems to have been well mastered in battles by modern engineers.

In 1926, Dr. D. J. McAdam, Jr., published the results of fatigue studies in which water had been used for thermal purposes. Dr. McAdam's conclusions were "additional experiments showed that this abnormality is not due to the thermal but to the chemical effect of water upon steel, and that this chemical action has unexpected influence on the fatigue resisting properties of the steels."[1] Later studies revealed that there is no plain carbon or alloy steel, other than the so-called stainless variety, which has a corrosion-fatigue value exceeding 25,000 lbs./in.[2] By corrosion-fatigue value or limit is meant the highest stress which a metal will endure indefinitely when subjected to repeated stresses and exposed simultaneously to the corrosive influence of a stream of water. "Indefinitely" is often accepted as meaning 10,000,000 cycles of stress under alternating flexure tests, on ferrous materials.

Visualize then the failings of even the strongest steels at the disposal of the metal users today. A steel with a tensile strength of 250,000 lbs./in.^{2} and a fatigue limit (in air) of 108,000 lbs./in.^{2} would appear to be a very safe steel for use under both static and dynamic loading. However, if there is corrosive action simultaneous with the dyamic loading, then the fatigue limit is lowered from 108,000 lbs./in.^{2} to a fatigue limit in water of 15,000 lbs./in.^{2} The corrosion-fatigue value of this particular steel is about 6% of its actual tensile strength.

This example proves the inutility of even the strongest steels available for certain uses and emphasizes the danger of corrosion-fatigue.

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Either one of two things or perhaps both must be done before safe loading can be put into members which are subject to the combined action of repeated loading and corrosion.

1. Corrosion must be eliminated in some way, or
2. Protective coatings which will protect the vulnerable material must be found.

These two possibilities were discussed in a previous paper[2] by the author. This same paper presented the protective values of hot dipped, sherardized and electrogalvanized zinc coatings against the combined action of corrosion and fatigue.

Since the zinc coatings offered a strong protection against corrosion-fatigue it was considered advisable to make a further study of protective platings. A study of the protection offered by cadmium plating was made and the results are contained in this article.

To study the effects of the embrittlement of steel by hydrogen gas during the pickling process previous to plating, various methods were used in the preparation of the surface for the platings. There are also included in this study some results obtained from electroplated zinc studies which augment the results of the cadmium platings.

CADMIUM AS A PROTECTION TO IRON

The position of cadmium in the electropotential series with respect to that of iron is rather doubtful. Measurements place cadmium just a few hundredths of a volt below iron in the electromotive series.

Zinc	— 0.76 volt
Iron	— 0.43 "
Cadmium	— 0.40 "

Thus from its potential cadmium offers no intrinsic protection to iron. Its protection is entirely dependent upon its imperviousness to the corroding medium. Thus with respect to its potential cadmium does not offer the protection that zinc does to the underlying iron. It is probable, however, that the electropotential position is not the only indication of the protective effects of one metal for another. There have been experiments which lead to the possible conclusion that at times cadmium does offer intrinsic protection to iron, although not to as great an extent as zinc does.

However, cadmium itself will not corrode nearly as rapidly as zinc. This fact is evidenced by the respective positions of each in the electropotential series. It is claimed that a cadmium coating is, at least in salt water, equal in protective value to one of zinc three times as thick.[3]

Moreover, since zinc and cadmium are the two common protective plating metals under ordinary conditions, it seemed advisable to study the behavior of cadmium plating when under corrosion-fatigue conditions.

EQUIPMENT AND MATERIAL

The R. R. Moore rotating beam type fatigue machine was used in all the tests. A few minor changes were made to the machine but only such as were necessary for the application of water to the specimens. The speed of the machine was 1750 r.p.m. and all the tests were run at this speed, in order that the results obtained might be comparable to those obtained by other investigators since ordinarily a speed ranging from 1400-1800 r.p.m. is used in fatigue studies. The standard R. R. Moore type specimen was used for all the tests with the ex-

ception that the fillets were made slightly larger than usual in order to facilitate polishing the fillets. With the usual fillets it was found to be difficult to polish in the fillets and rather than have an imperfect polish it was decided to enlarge the fillet. The diameter of the reduced section of the specimen was 0.300 in.

A fairly hard steel was used in all the tests in order that the range between the endurance limit in air and the fatigue-limit in water might be wide and afford a better opportunity for studying the protective effects of the cadmium platings. Accordingly a steel of the following analysis was chosen and was kindly supplied by the Bethlehem Steel Co.

Carbon	0.47%
Manganese	0.64%
Phosphorus	0.01%
Sulphur	0.035%

The steel was supplied in 7/8 in. round rods and was given the following heat treatments in the metallurgical laboratories of Lehigh University.

Heated to 1650° F., cooled in air.
Heated to 1575° F., quenched in water.
Heated to 1125° F., cooled in furnace.

In each heat treatment the rods were held at the required temperature for one hour before cooling. A microscopic examination checked the sorbitizing treatment. With this heat treatment the steel possessed the following properties:

Tensile Strength	105,500 lbs./in.^{2}
Proportional Limit	62,500 lbs./in.^{2}
Elastic Limit	62,500 lbs./in.^{2}
Yield Point	68,250 lbs./in.^{2}
Elongation (2 in.)	21%
Reduction of Area	48%
Modulus of Elasticity	29,100,000 lbs./in.^{2}

The machining of the specimens was done by the Bethlehem Steel Company and particular care was taken that too heavy cuts were not taken from the surface, to avoid possible hardening of the surface layers. The specimens were then polished through the following stages:

1. A longitudinal polish using No. 180 Aloxite cloth.
2. A longitudinal polish using No. 240 Aloxite cloth.
3. A circumferential polish using a canvas wheel with flour of emery in kerosene as an abrasive.
4. A longitudinal polish using No. 320 Aloxite cloth wetted with kerosene. The final polish was longitudinal in order to avoid any possible notch effect that a circumferential polish might afford.

The water used during the test was Bethlehem City tap water which is substantially a carbonate water and of which the following analysis is typical:

	P. p. m.		P. p. m.
Total Residue	134,500	Non-carbonate Hardness as $CaCO_3$	31.7
Fixed Residue	128,600	Chlorine as Chlorides	10.7
Loss on Ignition	5,900	Sulphates as Sulphur Trioxide	72.4
Total Hardness, Soap Method, as $CaCO_3$	80	Total Acidity	15.9
Permanent Hardness, Soap Method, as $CaCO_3$	67.1	Mineral Acidity	0.0
Temporary Hardness, by difference, as $CaCO_3$	12.9	Free Carbonic Acid	3.8
Oxygen Consumed	4.2	Silicon Dioxide	7.4
Alkalinity as $CaCO_3$	33.7	Iron and Aluminum Oxides	3.2
		Calcium Oxide	28.8
		Magnesium Oxide	6.0

The electroplating of the cadmium was done by the Udylite Process Company. Supplementing the corrosion-fatigue testing of cadmium plated steel, the embrittling effect of hydrogen upon steel was studied by varying the preparation of the plating surface. There were prepared three sets of test specimens, one set of each of the following:

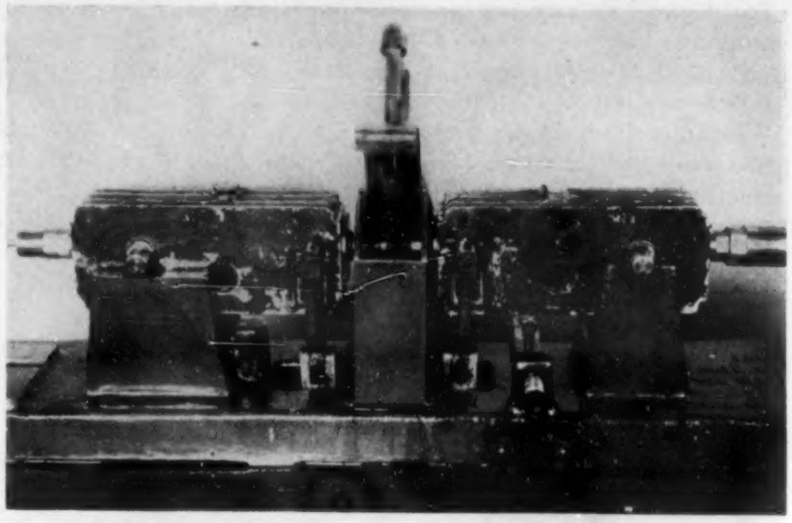
1. Surface degreased and cleaned with an organic solution before plating. Pickling was eliminated.
2. Regular commercial cadmium plating.
3. Same as 2. with a low temperature anneal to remove the absorbed hydrogen.

In the first set, the cleaning and degreasing was done with a very pure denatured alcohol.

The remaining two sets of specimens were cleaned in a solution of Wyandotte 5X cleaner with the work as cathode. The strength of the solution was six ounces of cleaner per gallon. The cleaning was done at a temperature of about 95° C. (203° F.) and a current density of 30 amps./ft.^{2} in a time of 3 minutes. The specimens rinsed in cold water and immersed for 2 minutes in a 10% by weight sulphuric acid solution containing 1% by volume of Rodine inhibitor (the Rodine content was figured in percent of concentrated sulphuric acid). The specimens were finally rinsed in cold water and immersed in the plating solution.

All of the three sets of specimens were plated similarly, namely, for 10 minutes at a current density of 15 amps./ft.^{2}; all in the same Udylite solution. The thickness of the platings after checking varied between .00022 and .00024 in. which is sufficiently close to call them equal thicknesses.

One set of the pickled and plated specimens was enclosed in tightly sealed tin cans and was heated in an oven for 24 hours at approximately 110° C. By this treatment it was hoped that the hydrogen would be removed. The oxidizing temperature of cadmium being about 250° C. (482° F.) it is certain that no oxidation of the cadmium occurred. There were, however, what appeared to be extremely fine bubbles in the plating, indicating a slight porosity of the cadmium due to the evolution of hydrogen.



Fatigue Machine set up for Corrosion Work.

The electroplating of the zinc was done in the Bell Telephone Laboratories. Again one set of specimens were cleaned with an organic compound. Alcohol and ether were used as a preparation for plating.

The other set was treated in the commercial manner. The specimens were degreased and cleaned in a 30 g./l. solution of Wyandotte compound. The work was used as the cathode and the temperature of the operation was between 80° and 90° C. (170° and 194° F.). The time of cleaning was 2 minutes. Following the cleaning, the specimens were rinsed in cold water and dipped for one minute in bright acid dip of the following concentration:

Conc. sulphuric acid	12 parts
" nitric acid	4 parts
Water	1 part

The specimens were again washed and then dipped in a 30 g./l. sodium cyanide solution for 2 minutes. Following a cold and hot water wash, the specimens were plated in a cyanide bath. The average weight of the zinc coating was 136.6 mg./in.^{2} which gave a thickness of about .0011 in. There were no specimens annealed.

PROCEDURE OF TEST

The results of uncoated specimens run in air and water are shown in Fig. 1. Each point represents a specimen which was broken with the exception of those marked as removed. The specimens which were run in air were cleaned thoroughly with alcohol and were given a thin coating of oil. The fatigue limit of the bare polished steel specimen in air is shown to be about 60,500 lbs./in.^{2}. The uncoated specimens which were run in water were also cleaned very carefully with alcohol to remove any grease that might be on the surface of the specimens and might restrict the water from reaching the surface of the steel. The stream of water was applied at right angles to the

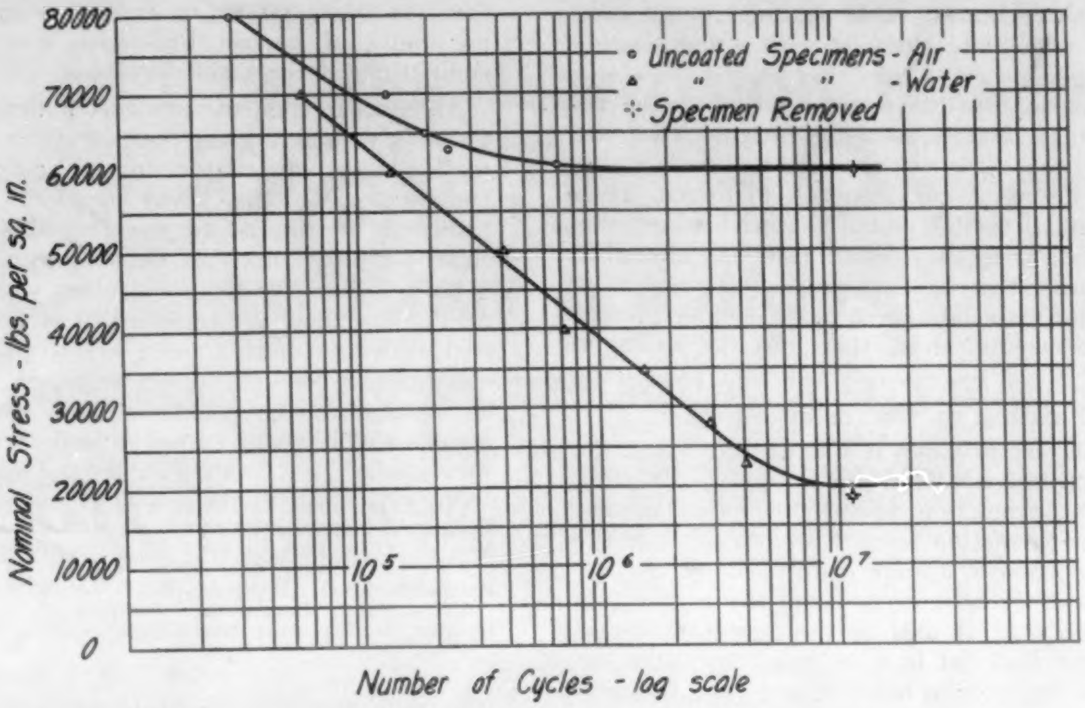


Fig. 1

specimens for a distance of about ¾ in. in its region of maximum stress. There was no difficulty with the specimens breaking in any place other than the region of maximum stress. The temperature of the water varied from 65° to 75° F. The corrosion-fatigue limit of the uncoated steel in plain water was about 20,000 lbs./in.²

The cadmium and zinc coated specimens were run in water in exactly the same manner as the uncoated specimens. The results of the cadmium coated specimens are shown in Fig. 2 and those of the zinc coated specimens in Fig. 3.

The fatigue values in water for the tested material are as follows:

Cadmium plated steel —organic solvent	42,000 lbs./in.²
Commercial cadmium plated steel	46,000 lbs./in.²
Commercial cadmium plated steel—annealed	46,000 lbs./in.²
Zinc plated steel —organic solvent	60,000 lbs./in.²
Commercial zinc plated steel	49,000 lbs./in.²

DISCUSSION OF RESULTS

It would be preferable to discuss the results obtained from these tests under two divisions as outlined in the title of the article:

A. Cadmium Coatings vs. Corrosion-Fatigue

As shown in Table I, cadmium plating offers a very considerable protection toward the effects of corrosion-fatigue. There does not appear to be much choice among the three sets of results—the variation in percentage protection only being

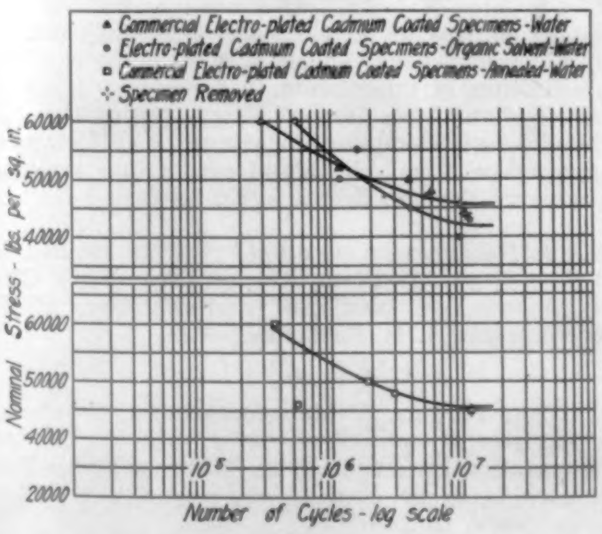
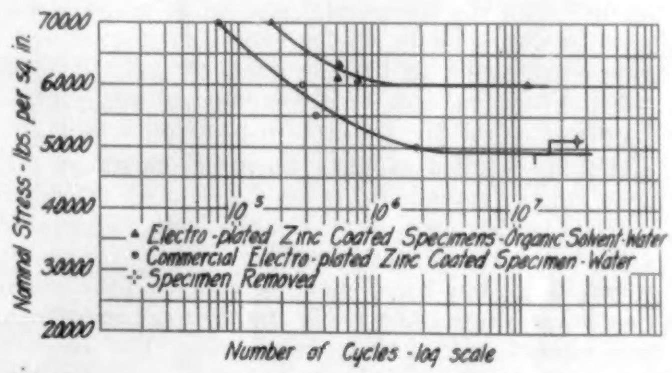


Fig. 2

about 10% in favor of the commercially coated specimens. From previous experiments upon the zinc coatings[2] it was expected that cadmium plated material which is not subjected to a hydrogen embrittlement by pickling would offer more resistance toward corrosion-fatigue than commercially plated material. This fact in this experiment at least was not proven and the result is quantitatively shown in Table I. However, it is very possible that a truly impervious condition of the coating was not obtained since the best possible plating was not secured because the usual plating surface roughened by acid dip was not offered toward the deposition of the cadmium. There are at least two possible excuses for a not completely impervious coating:

Fig. 3



a. The specimens might not have been cleaned of grease, the last microscopic traces.

b. The surface presented, even if perfectly degreased and cleaned, was not the most conducive surface for the best cadmium plating.

It will be noticed that no difference in corrosion-fatigue resistance appears in the commercially plated specimens, whether or not the material is annealed. This might be expected since the hydrogen absorbed during pickling probably diffused from the surface of the unannealed specimens before test work was begun. It is well established that in time any hydrogen absorbed in pickling will at atmospheric temperature diffuse to the surface and escape from the material. The annealing simply accelerates the diffusion process.

It must be remembered, however, that the cadmium platings used were .00022 in. thick. It is very possible that had heavier

TABLE I

	Fatigue Limit air	Fatigue Limit water	Percentage Protection*
Uncoated steel	60,500		
Uncoated steel		20,000	
Cadmium plated — organic solvent		42,000	54.4%
Cadmium plated — commercial		46,000	64.2%
Cadmium plated — commercial annealed		46,000	64.2%
Zinc plated — organic solvent		60,000	98.9%
Zinc plated — commercial		49,000	71.5%

*The percentage protection represents the percentage approach toward a perfect resistance against corrosion. If the corrosion-fatigue limit were increased to coincide with the fatigue limit in air, corrosion would be eliminated and the protection be 100%.

As an example the rise in such a perfect condition measured by a stress would be 60,500-20,000 lb./in.². If the plated material offered a corrosion-fatigue limit of 40,000 lb./in.²—then its protection would be 40,000-20,000 lb./in.² and its percentage protection $\frac{40{,}000-20{,}000}{60{,}500-20{,}000}$ or 49.5%.

coatings been used, the resistance value obtained would compare more favorably with those obtained with a zinc coating of .0011.

It was not the purpose of this paper to include the resistance of zinc platings toward corrosion-fatigue. They are only included in that they form evidence for the second purpose of the paper: the effect of absorbed hydrogen. It is well to note, however, that the plated material which was cleaned and degreased with an organic material offered a practically perfect protection to the underlying steel. The commercially plated zinc material offered but a slightly greater protection to the underlying metal than did the cadmium coatings.

B. Effect of Pickling vs. Corrosion-Fatigue

At the outset of the test program it was expected that the plated specimens which had not been pickled prior to plating would afford the best protection against corrosion accompanied by fatigue. The prediction seemed warranted since the surface of the pickled steel is always embrittled by the hydrogen absorbed. This embrittled area, being the region furthest distant from the neutral axis of the specimen, would particularly weaken the material in a fatigue test where the strain is a maximum in the regions most distant from the neutral axis. If the surface to be plated were cleaned by a process wherein no embrittlement would occur and if the plated material were absolutely protective, then the fatigue limit in water should coincide with that in air.

As shown in Fig. 3, the perfect protection was offered to the base metal by a zinc coating on a surface previously cleaned only with an organic solvent. With a zinc coating of the same weight where the usual pickling operation was used preparatory to plating, the corrosion-fatigue limit decreased from 60,000 lbs./in.^{2} in the perfect protection to 49,000 lbs./in.^{2} with the commercial method of plating. Since the two platings were exactly similar and since zinc offered a high intrinsic protection to iron, it must be concluded that the absorbed hydrogen and its accompanying weakening effect was the direct cause for the drop in protection value.

The same series of tests upon the cadmium coated specimens fails to reveal similar results. The set of cadmium plated material which had been cleaned with an organic solvent showed a corrosion-fatigue value slightly lower than the set prepared by the usual pickling process previous to plating. This lower value is probably due to the condition of the surface offered to cadmium for plating. The condition of the surface since it was not roughened by acid dip was not that which is favorable for best cadmium deposition with the result that protective value was not quite that of the better cadmium coatings, which previously to plating had been pickled.

The similarity in the results obtained by testing pickled and plated specimens in both annealed and unannealed conditions seems to indicate that the embrittlement remained in the steel even after the hydrogen had been removed by annealing. It is very possible that the absorbed hydrogen might also have been removed from the unannealed specimens since they were tested several months after plating; a time which might have allowed the gas to diffuse from the surface of the plated material. From the results obtained in test, the annealing does not improve the corrosion-fatigue conditions of the underlying metal. This fact indicates that the deleterious effect is not due particularly to the absorbed gas but to some condition in the metal which is caused by the absorbed gas and which condition remains even after the gas has been removed.

Again it must be recognized that the cadmium coatings were less heavy than the zinc coatings so a comparison would be rather unfair.

CONCLUSIONS

The results in Table I show that each of the platings used gave a very decided protection to the base metal and indicate that the problem of protective plating against corrosion-fatigue is one of rare importance. It has been shown that both cadmium and zinc offer very good protection and it is probable that there are other metals which will present as good if not better "water-proofing" for steel.

The deleterious effect of pickling upon the corrosion-fatigue limit of steel is very definite. Regardless of the protective metal used, the corrosion-fatigue limit of the metal ranged from 46,000-49,000 lbs./in.^{2}. This seems to indicate that the possibility of perfect protection was only thwarted by the embrittling of the pickled surface.

An effort to eliminate absorbed hydrogen by cleaning and degreasing with an organic compound rewarded by a perfect protection in the case of the zinc coating. The similarly prepared cadmium coated specimens were not as successful and its failure is attributed to the fact that the cadmium plating could not adapt itself to the surface presented for deposition. With a better surface preparation wherein all hydrogen producing materials are excluded, it is believed that a cadmium coating would offer a quite better protection against corrosion-fatigue conditions. It is hoped that this problem of eliminating a pickling bath for some particular purposes which involve simultaneous corrosion and fatigue will be given further study.

REFERENCES

[1] D. J. McAdam, Jr., Stress-Strain-Cycle Relationship and Corrosion-Fatigue of Metals. *Proceedings American Society for Testing Materials*, Vol. 26, 1926, Part II, page 224.

[2] W. E. Harvey, Zinc as a Protective Coating Against Corrosion-Fatigue of Steel. *Metals & Alloys*, Vol. 1, April, 1930, page 458.

[3] Blum and Hogaboom, Principles of Electroplating and Electroforming. McGraw-Hill Book Company, New York, 1930.

◈ ◈ ◈

Battelle Memorial Institute has coöperated with the Ohio State University Engineering Experiment Station in an investigation of the White process of carbonization of coal with Floyd B. Hobart, fuel chemist for the Battelle Memorial Institute, and D. J. Demorest, professor of metallurgy at the University, as investigators. These men have compiled the results of the tests which have been published as Bulletin 65 of the Station and entitled "Tests on the Continuous Carbonization of Finely Crushed Coal by Radiant Heat."

Coals from Ohio, West Virginia, and Illinois were used for the tests and dropped through the one-ton vertical retort of the Station. The by-product purification and recovery equipment of the Station was modified for the experiments. Coke, gas, and tar are the chief products of the process.

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The Lead Industries Association has approved a new standard of lead pipe sizes which is being adopted by the principal manufacturers as an aid to consumers. In addition to eliminating numerous variations in pipe sizes now found among lead pipe manufacturers, an outstanding feature of the new standard is that all sizes of lead pipe in the A, AA and AAA classifications, (or "Strong," "Extra Strong" and "Double Extra Strong") will safely withstand constant cold water pressures of 50, 75 and 100 lbs./in.,^{2} respectively.

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The Foundry Equipment Company, Cleveland, Ohio, manufacturers of Coleman Core and Mold Ovens and Swartwout Industrial Ovens, has purchased the business of the McCann-Harrison Co. The business will be operated as the McCann-Harrison Division of The Foundry Equipment Company, with main offices and plant located at 1831 Columbus Road, Cleveland, Ohio.

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The Aluminum Company of America and I. G. Farbenindustrie A.-G., of Germany, have joined forces to develop the commercial possibilities of magnesium.

The two organizations have formed a new corporation, the Magnesium Development Company, incorporated in Delaware, which will make recent discoveries about magnesium available to American industry through license agreements and instruction.

The Magnesium Development Company will be headed by Walter H. Duisberg, of 521 Fifth Avenue, New York City. The board of directors will consist of representatives of the Aluminum Company and I. G. Farbenindustrie.

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The Canton Drop Forging & Manufacturing Company of Canton, Ohio, has recently placed an order with the Surface Combustion Corporation for a Slot Type Diffusion Forge Furnace. This furnace is to be used to end-heat square billets in continuous operation to 2200° F.

◈ ◈ ◈

Surface Combustion Corporation has contracted to install two continuous walking beam furnaces for heating packs and pairs in the Aliquippa Tin Mills of Jones & Laughlin Steel Corporation, and another walking beam pack furnace for the Tennessee Coal, Iron and Railroad Company, Birmingham, Alabama.

Effect of pH on the Corrosion Products and Corrosion Rate of Zinc in Oxygenated Aqueous Solutions†

By B. E. ROETHELI, G. L. COX* AND W. B. LITTREAL**

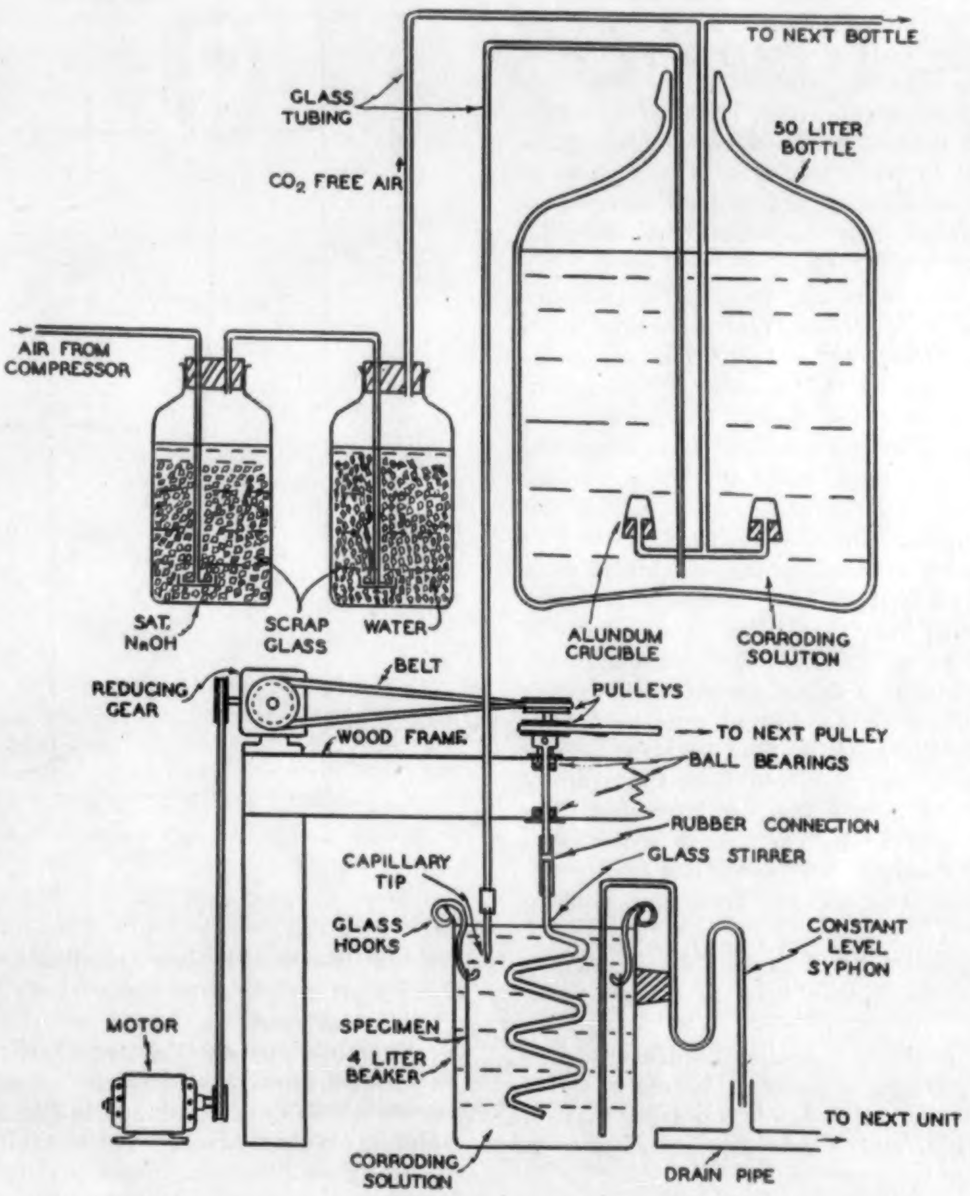
INTRODUCTION

COMMERCIAL structural metals are produced from ores (such as oxides, sulphides, etc.) which are thermodynamically more stable than the metals themselves, and there is a constant tendency for the metals to revert to a form identical with, or similar to, that found in nature. Unfortunately the stable forms generally possess physical and mechanical properties which render them unsuitable for structural purposes.

Were the reversion to the stable forms rapid, the use of metals as structural materials might be prevented entirely, but fortunately, while oftentimes great tendencies exist to assume the stable state, the rate of reversion may be extremely low and may depend to a great extent on the external conditions to which the metal is exposed.

The process of corrosion in neutral or nearly neutral solutions is generally accompanied by the formation, on the metal surface, of films of oxides or hydrous oxides which tend to serve as barriers to the attack of the metal by the most common corroding constituent present in solutions; namely, oxygen. Frequently, these films are so effective that rapid corrosion proceeds for only a short time, and when the insulating action of the films becomes a predominantly controlling factor, further corrosion is either prevented, or the rate is reduced to a small and oftentimes negligible value. The effect of films has been studied in detail by several investigators [5, 9, 11, 12, 16] and in all cases the permanence of and the physical characteristics of the films were seen to be of considerable importance in determining the ultimate rates of corrosion.

In view of the fact that the films tending to retard corrosion are generally of the hydrous oxide types, and whose solubilities and physical characteristics are markedly influenced by the acidity and alkalinity of the solutions it was believed of interest to study the corrosion rate of a typical metal, zinc, in solutions having different pH values. In the case of zinc an insight to the importance of film solubilities must necessarily be shown since zinc hydroxide is an amphoteric compound whose solubility is increased both by high acidity and high alkalinity.



For the purpose of correlating corrosion rate data with the solubility of zinc hydroxide, a literature survey was made from which it was concluded that the solubility of zinc hydroxide was not a very definitely determinable quantity and that it depended on various factors such as degree of hydration, crystalline structure, colloidal dispersion and the presence of other salts. [2, 3, 4, 6, 13, 14, 15, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 39, 40, 42] It was therefore believed advisable to investigate the actual corrosion rates and to make supplementary examinations of the corrosion products in order to establish the pH ranges in which the corrosion product afforded protection and those in which no protection was to be expected.

APPARATUS AND EXPERIMENTAL WORK

The method of testing the corrosion rate of zinc in solutions of different pH involved (1) the maintenance of constant pH values in the corroding media, (2) saturation of the liquid with oxygen, (3) elimination of dissolved carbon dioxide in the air for aeration, (4) maintenance of constant temperature. The essential features of the apparatus are indicated diagrammatically in Fig. 1. One unit of a system of eight similar units is sketched in detail.

The method of carrying out the corrosion rate determinations was as follows: The 50-liter bottle was filled with a solution of the approximate pH desired, made from neutral water,[a] hydrochloric acid, or sodium hydroxide, using the relation between pH and normality as given in Van Nostrand's Chemical

†Based on a thesis submitted by W. B. Littreal in partial fulfillment of the requirements for the degree of Master of Science, 1930. Research Laboratory of Applied Chemistry, Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

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**Present address: Standard Oil Co. of Indiana, Whiting, Indiana.

[a]The water was distilled, and the pH of the water taken from the tap was so near 7 that it could accurately be called neutral.

Annual.[39, b] Air from a compressor was bubbled through a large bottle containing a saturated solution of sodium hydroxide to remove any carbon dioxide, the presence of which is known to be a variable in the corrosion of zinc[1] by water—and which would also alter the pH of the solution. The air was subsequently passed through a similar bottle containing distilled water to remove alkali which might have been entrained in the air leaving the first bottle. The absorption bottles were filled with broken glass to afford a large area for contact between the gas and liquid. The air free from carbon dioxide was passed through four alundum crucibles in the reservoir bottle to permit rapid saturation and maintenance of saturation of the liquid with air.

The solutions were aerated as described for approximately one hour before the tests were begun. The liquids were fed to the test beakers through glass tubes, fitted at the lower ends with fine capillary tips calibrated to give an average flow for 24 hours of about 2 liters per hour. Subsequently, the liquids passed through constant level siphons to the drain. The pH's of the solution in the beakers were determined twice daily to check their constancy. Both indicator and electrometric methods were employed in the pH measurements. For pH values near the neutral point (pH of 5 to 9) the pH's in the beakers were found to be slightly greater on the acid side and slightly less on the alkaline side, than those of the solutions in the large reservoir bottles. There were no appreciable differences in the solutions of pH's less than 5 and those of pH's greater than 9.[c] The values of pH plotted were those of the solutions in the beakers. The temperature of the solutions was maintained at 30° ± 1° C.

The specimens for the tests were cut from 26 gage rolled C.P. zinc supplied by the New Jersey Zinc Company of a zinc content of more than 99.99% by weight.[d] The specimens were supported from the rims of the beakers by means of glass hooks so constructed that the metal specimens were supported away from the sides of the beakers, thus permitting the solutions to circulate past both sides of the specimens. Four check specimens were used for each run, insuring that a fair average rate of corrosion for each particular value of pH could be obtained. Before immersion, the specimens were marked for identification, pickled in 10% hydrochloric acid, washed, polished lightly with very fine steel wool, rinsed in alcohol, dried and weighed. Upon removal, the specimens were cleaned in a similar manner, using a definite number of strokes with the steel wool. After the second weighing, another polishing was made using exactly the same number of strokes, and the loss in weight so obtained was deducted from the original loss to give more nearly the actual loss by corrosion. The polishing correction was found to be very small when compared with the gross loss in weight. The deviation among the four specimens for each run was not 5% from the average value.

The periods of testing varied from 5 to 30 days so that in all solutions substantially the same loss in weight was obtained.[e]

The solutions within the beakers were kept uniformly agitated by means of glass stirrers, connected to steel shafts which fitted into the wooden frame through ball bearing thrusts to maintain smooth operation, and which were rotated at a speed of 120 revolutions per minute.

[b]The pH of a solution may be expressed as a function of normality, which function approximates a linear relationship on semilogarithmic coordinates. Such a curve was used to make up the solution approximately to the pH desired. For the highest pH value used extrapolation of the curve was necessary.

[c]The colorimetric results were found to be in agreement with the electrometric within ± 0.1 of a pH unit at pH values below 6 and above 8, although the latter were used in making up the plot (Fig. 2). At pH's from 6 to 8 it was necessary to use the values obtained from colorimetric determinations because of the long time required to reach an equilibrium potential when the electrometric method was used. The length of time required permitted absorption of CO_2 and hence caused erroneous values in pH measurements.

[d]Analysis: Zinc 99.991+%
Iron 0.0025%
Lead 0.0025%
Cadmium 0.003 %
Arsenic 0.00005%

[e]The criticism might be raised that the results would not show the true rate of corrosion for all the specimens owing to the high initial corrosion rates. The period of high corrosion rate during which films are built up has been found to be of very short duration[5] so that in the solutions in which films are formed the period of 30 days seemed long enough to warrant attributing most of the loss in weight to corrosion as controlled by the secondary diffusion reaction.

RESULTS AND DISCUSSION

The results of this investigation are shown graphically in Fig. 2 in which the ordinates represent average overall penetrations in centimeters per year at 30° C.;[f] and the abscissas the measured pH values of the corroding solutions. In the figure, four divisions are indicated which represent the effects of four different combinations of factors upon the corrosion rates of zinc in aqueous solutions having different pH values. The divisions are designated in the figure as acidic film-dissolving, (pH<6), stable film (ph>6<12.5), dilute alkaline film-dissolving, (pH 12.5-13.5) and strongly alkaline, film-dissolving (pH 13.5) ranges. These ranges correspond to regions

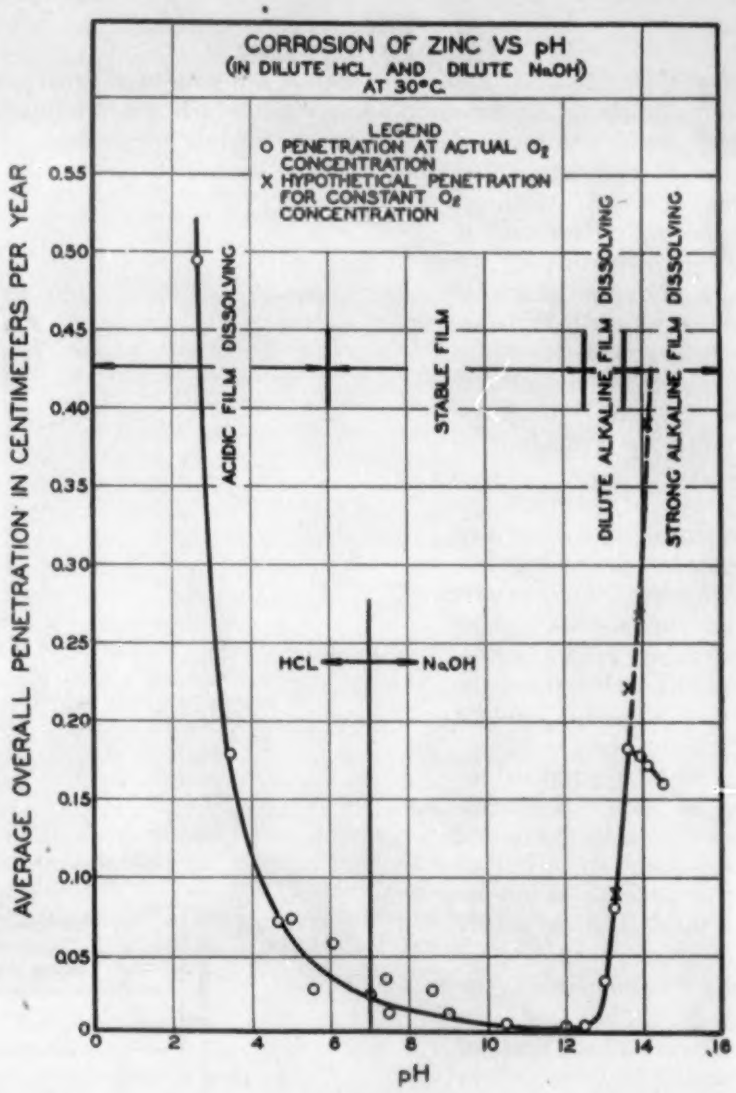

Fig. 2

of high diminishing, low and diminishing, higher and increasing, and high and diminishing corrosion rates, respectively, as the pH is increased.

Examinations of the metal specimens removed from the solutions showed a uniform attack on all and no films on those which were immersed in the solutions classified as acidic film dissolving (except for a slight film at a pH of 5) and strongly alkaline film dissolving. In these ranges three factors have probably influenced the ultimate corrosion rates; namely, the hydrogen ion concentration, hydroxyl ion concentration, and the solubility of oxygen. Inasmuch as the solubility of oxygen in the acidic range investigated was substantially the same in all cases, the corrosion due to depolarization of oxygen in all probabilities was a constant quantity[g] so that the increasing availability of hydrogen ions necessary to shift the equilibrium of the reaction $2H \rightleftharpoons H_2$ to the right was the chief factor in increasing the corrosion rate as the pH decreased. In the strongly alkaline film-dissolving range, however, the situation became extremely complex owing to the possible oc-

[f]This is below the temperature at which marked changes in the physical properties of the film commence to exert a tremendous influence upon the corrosion rate.[7]

[g]All the oxygen is assumed to be consumed as soon as it reaches the metal surface and when external conditions are the same the rate of depolarization on film free surfaces depends upon the solubility of the oxygen in the corroding medium. The conductivity effect probably did not vary much since in all solutions in this range the conductivity is quite high.

currence of several distinct reactions singly or simultaneously. These reactions are listed herewith:

(1) $Zn + 2H_2O = Zn(OH)_2 + 2H$
(2) $2H + 1/2\,O_2 = H_2O$
(3) $2H = H_2$
(4) $Zn(OH)_2 + 2NaOH = Na_2ZnO_2 + 2H_2O$
(5) $Zn + 2NaOH = Na_2ZnO_2 + 2H$

In dilute alkaline solutions where no hydrogen evolution took place reaction (1) was undoubtedly the primary reaction and reaction (2) was the cause of a continued disturbance of the equilibrium by removal of atomic hydrogen (H). As the pH was increased, a reaction such as No. (4) probably was responsible for the absence of films of zinc hydroxide on the metal surface and the resulting reduced resistance to the diffusion of oxygen permitted a more rapid transfer of the depolarizing oxygen to the metal surface and hence more rapid progress of reaction (2). As the pH was increased still further,

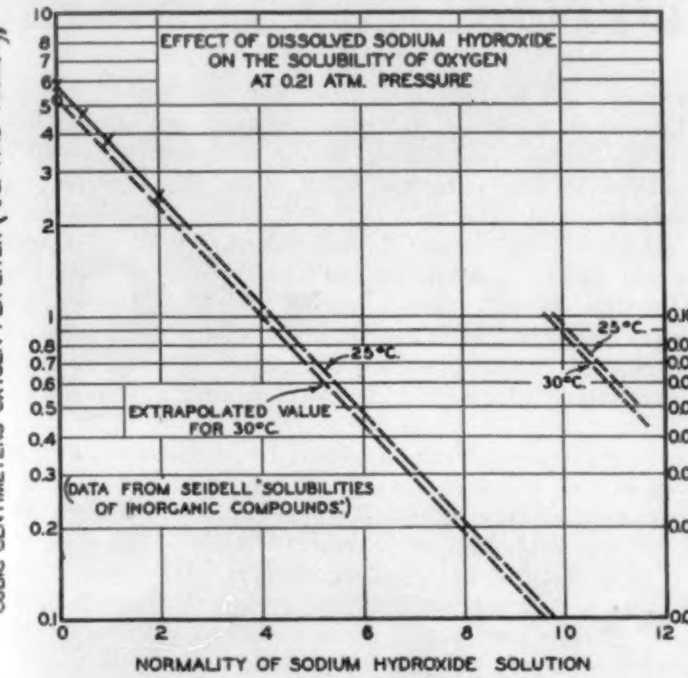

Fig. 3

hydrogen was observed to evolve slowly from the metal surface. This suggested the possibility of a reaction such as (5), however, an analysis will show that this is merely the summation of reactions (1) and (4) and that the process may be considered as having occurred, as in the former cases, in two steps. The differences between this case and those in more dilute alkaline solutions evidently were due to the fact that the metallic ion concentration was reduced so much by reaction (4) that a potential was obtained which was sufficiently high to permit, in a strong electrolyte, the formation of atomic hydrogen at rates such that the oxygen present no longer sufficed for its removal by reaction No. (2), and so reaction No. (3) commenced to become important. The fact that the presence of oxygen was still of prime importance may be seen from an examination of Fig. 2 in which the corrosion rate is observed to decrease in solutions of high pH. If the corrosion rate depended solely upon the effect of the alkalinity upon the potential and the consequent ease of hydrogen gas formation the corrosion rate should increase with increasing pH. If, however, the corrosion rate were dependent upon both the depolarization by hydrogen gas formation and by oxygen the rate would still be increased in solutions of higher pH if the oxygen concentration remained constant. On the other hand, were the solubility of oxygen to diminish, three possibilities would arise, (a) the corrosion rate would increase because of the greater importance of reaction (3), (b) the corrosion rate would be constant owing to an exact balance between the increased rate of reaction No. (3) and the decreased rate of reaction No. (2). (c) The corrosion rate would diminish because of the greater importance of reaction (2). Evidently the last mentioned case was true in this investigation. An examination of Fig. 3[38] indicates a great diminution of the oxygen solubility as the pH[h] is increased and a hypothetical extension of the corrosion rate curve computed on a basis that corrosion rates are proportional to the oxygen concentration[i] indicates that much higher corrosion rates would have been observed had not the oxygen solubility diminished. In both the acidic and strongly alkaline film-dissolving ranges, therefore, the high corrosion rates may be attributed in a large measure to the accessibility of hydrogen ions, hydroxyl ions, and oxygen to the metal surface because of the absence of films and the differences in the corrosion rates in these two ranges is due to the differences in the methods by which hydrogen (H) is removed from the surface, i. e. primarily by hydrogen evolution in the acid solutions, and by oxygen in strongly alkaline solutions.

In the stable film range, where corrosion rates are relatively low, films are present in all cases. The differences in corrosion rates, however, may not be satisfactorily explained merely upon the basis of film solubility in solutions of different pH values since the most generally reported values for the solubility product $(Zn^{++})\ (OH^-)^2$ of zinc hydroxide [10, 19, 30, 34, 35] 1 to 4×10^{-14} which when merely considered from a pH viewpoint are much too high for precipitation of the hydroxide in some of the solutions of low pH. Values of this magnitude postulate a zinc ion concentration of 1 to 4×10^4 mols per liter[j] for the precipitation of the hydroxide at a pH of 5, at which value traces of film were present. However, the values indicated for the solubility products lend themselves to a successful application in case of the results of this investigation when the effect of the mechanism of corrosion on the pH of the liquid film on the metal is taken into consideration.

During the process of electrochemical corrosion, hydrogen ions leave the liquid film adjacent to the metal and metallic ions enter the film so that the film is an electrically balanced system. The diminution of the number of hydrogen ions, leaves an excess of hydroxyl ions in the film. The pH in the film thus increases and because of the high initial corrosion rate[5] may reach values high enough to permit the precipitation of the insoluble hydroxide at a relatively low metallic ion concentration even though the pH of the solution outside of the liquid film is much lower. Apparently, the importance of the pH value of the main body of the solution rests in its effect upon the production of a hydroxyl ion gradient from the film to the solution and its consequent effectiveness in causing a depletion of the hydroxyl ion concentration in the liquid film adjacent to the metal. In order for the diffusion gradient to be the sole factor in determining the critical precipitation point, the other factors influencing diffusion such as liquid velocity, diffusion resistance of the films, and the specific diffusion rate must all remain constant. Undoubtedly, in the apparatus used this is not rigorously the case and variations in any of these factors could have produced such deviations from the smooth corrosion rate curve as are shown. The equipment as used does not permit absolute control of the liquid velocity past the plate, nor are the corrosion products uniform as regards density, or perhaps even composition, since they appear to be more compact as the pH is increased.

In the dilute alkaline film-dissolving range, the phenomena observed may be attributed to the joint effect of the increasing stability of soluble zincates and the high solubility of oxygen. As the pH increases the zinc hydroxide becomes soluble in the alkali and the tendency for formation of protective films is reduced. In this case the liberation of hydroxyl ions by the corrosion reactions does not cause the precipitation of the hydroxide and it is even conceivable that the additional hydroxyl ion concentration may cause a solution of the film at pH's below that necessary for the solution of zinc hydroxide.[k] At the pH values in this range the solubility of oxygen is high, so that the high corrosion rate is undoubtedly dependent upon the ease with which oxygen can penetrate the corrosion product film and, as may be seen from the curve, the greater the tendency to form zincates (the less film there is present) the higher the corrosion rate becomes until a pH value is reached at which the oxygen solubility begins to decrease.

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[h] In this region very large increases in molal concentrations effect only a small increase in pH.

[i] For steel the corrosion rate is proportional to the oxygen concentration up to oxygen concentrations of 5.5 cubic centimeters per liter.[8]

[j] The entire quantity of zinc used in this investigation would be insufficient to produce a concentration of this magnitude.

[k] The value for the zinc hydroxide solubility in alkalies has not been definitely established in view of the possibilities of formation of colloidal particles, acid zincates and zincates, so that this point cannot readily be proved. 2, 13, 14, 15, 17, 18, 20, 21, 23, 25, 26, 27, 28, 31, 42.

This investigation, as may be seen in the discussion above, has indicated that it is practically impossible to interpret results upon the basis of single factors such as pH alone and while the results presented show a stable film range for pH values from 6 to 12.5 the results of investigations under different external conditions such as different temperature, or turbulence might show appreciable departures from the limiting pH values found here and similarly, the limiting values for the other ranges could also be changed if conditions were altered. For this reason the results of this investigation should be accepted with the understanding that variations in the external conditions might cause increases or decreases in the corrosion rates and that in a universal sense the condition of low or negligible corrosion probably lies between pH values of 6 to 8 as minima and 11 as a maximum.

CONCLUSIONS

1. Zinc is rapidly corroded by aerated solutions whose pH is less than 6 or greater than 12.5 owing to the high solubility of the corrosion product formed and the ease with which hydrogen ions, hydroxyl ions, or oxygen can reach the metal surface.

2. In solutions having pH values from 6 to 12.5 the low corrosion rates are attributed to the presence of dense and adherent protective corrosion product films.

3. Insoluble corrosion products may precipitate on the metal at pH values as low as 5 despite the extremely high concentrations of metal ion required for their precipitation in the solution, due most probably to the production of high pH's in the liquid films adjacent to the metal by the corrosion process.

4. Variations in external factors such as turbulence may cause variations in the pH values indicated as the limits of the four ranges (acidic film-dissolving, stable film, dilute alkaline film-dissolving, and strongly alkaline film-dissolving) because of their effect upon the rate of diffusion of hydroxyl ions from the liquid film, adjacent to the metal, to the solution.

ACKNOWLEDGMENT

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EDITORIAL COMMENT

(Continued from Page 55)

is scarcely less blatant than the usual newspaper account.

The actual work, on precipitation-hardened copper-base alloys with nickel and silicon, would probably prove to be of some interest and scientific value, since the general program is understood to have been laid out, during the research worker's previous employment in the laboratory of a progressive firm, for him to carry on at the school. But the work had not yet been published by any scientific society or journal, avid as they are for accounts of worth while scientific advances. Thus, non-technical "blah" preceded scientific publication, and what little technical information is hinted at certainly doesn't sound new to us.

The non-technical write-up refers to previous work of others in this line of research in a very deprecating vein, and gives the impression that nothing worthwhile was known in this field till the "Aladdin of Industry" being publicized, turned the blazing light of his intellect upon it, and that his achievement was a vast one, redounding greatly to the credit of the school. "Such an alloy had been produced previously, but no critical reports on its metallurgy had been made nor had it been adapted to industry," is one specific statement. The article's sub-head is "A university research laboratory makes over an industry five thousand years old." These are pretty sweeping statements, scarcely in line with the traditional modesty of scientists.

The inclusion of a picture of the president of the school makes the account appear official and as if sanctioned by the school. If it was so sanctioned, and if the school authorities looked upon it as desirable publicity, they might be disillusioned could they hear the word-of-mouth comments of the metallurgical world. Such publicity may be a boomerang, and tend to injure the individual scientists so publicized, and to depreciate the institution itself, rather than to help either.

More than one state school has been guilty of letting publicity get out which claimed that its research work revolutionized a metallurgical industry of the state, when its own contribution was very slim and major credit belonged elsewhere. The aim of the sweeping claims in non-technical publicity in such cases seems often to be to impress the legislators at a time when appropriations for the school are up for discussion. Or, the object may be to attract students. But we have never heard of any increase in appropriations that was traceable to such publicity. Most scientists would advise their young friends to choose a school that does not go in for flamboyant non-technical publicity, and whose professors and administrators neither play the braggart and try to hog more credit than should belong to them, nor allow a reporter to do it for them.

The "hard copper" article is not the only example of offense against good taste in metallurgical matters, but it is so outstanding a case of misdirected zeal and poor judgment in institutional publicity that it might be taken as an example to be avoided by those schools that want the complete respect of the scientific world. For their own good, the scientists at such schools should try to hold the reporter and the publicity agent in check. There is a price to be paid for publicity that violates good taste. It should be possible to interest the layman without disgusting other scientists.—H. W. Gillett

Effect of Crystal Size on Physical Properties of Tin-base Babbitts

By ERNEST B. DRAKE*

THIS investigation is a continuation of the work begun on tin base babbitts during the summer of 1930, the results of which were published in METALS & ALLOYS for January 1931.

The purpose of this part of the investigation was, first: to determine whether the crystal size, as revealed by macroetching, could be controlled by controlling the casting temperature and the mold temperature; and second, whether there is any connection between crystal size and physical properties in babbitts, similar to what is found in other alloys. It was hoped the casting technique for connecting rod and main bearings for internal combustion engines might be improved by regulating the crystal size of the babbitts.

The laboratory work consisted of the following:

1. Making a series of thin, flat castings at a number of casting and mold temperatures to illustrate the change in crystal size.
2. Preparation of specimens for micro and macroexamination from the above castings.
3. Determination of hardness of the above castings by Rockwell, Vickers, and microcharacter machines.
4. Making a series of cylindrical castings and preparing specimens from them for compressive strength tests.
5 Making compressive strength determinations.
6. Macroexamination of compressive strength specimens before and after they were subjected to the test.

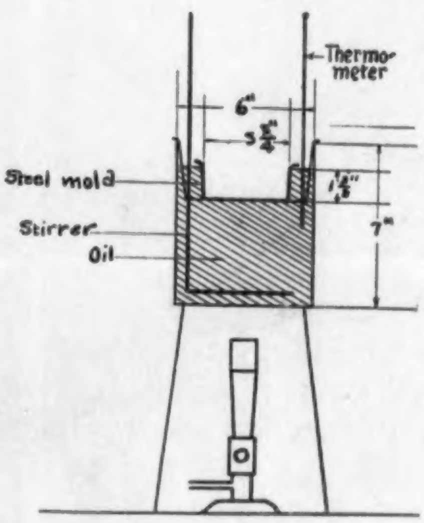

Fig. 1

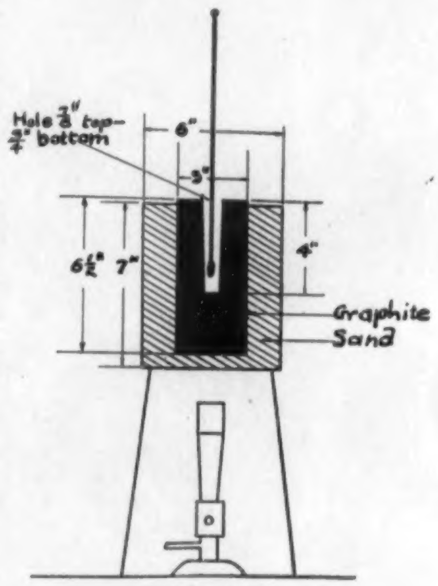

Fig. 2

It was thought best to make the castings for the study of crystal size thin in order to more nearly duplicate the conditions existing in main and connecting rod bearings; and therefore the mold used was a steel cup 1⅜ inches deep by about 3¾ inches diameter immersed in an oil bath. Fig. 1. Enough babbitt was poured in to make a casting about ¼" thick, care being taken to pour the metal into the mold as quickly as possible in every case.

All the metal used in these experiments was new metal which had been furnished by the manufacturer to an automobile company and which had the approximate composition: 85% Sn; 7.5% Cu; 7.5% Sb. It was melted in a clay crucible in an electric furnace equipped with a base metal thermocouple and a pyrometer, the errors in the readings of which were probably not greater than ± 5° F. The oil bath was stirred, and the temperature was read from a thermometer reading directly to 2° F., and when both the mold temperature and the casting temperature had been practically constant for 10 minutes the casting was made. Just enough metal was used each time to make one casting. The castings made at the higher mold temperatures were left in the mold for say 30 minutes to make sure that the metal was completely frozen before it was removed from the mold.

Eight different casting temperatures were used, viz.: 750°, 800°, 825°, 850°, 875°, 900°, 950°, and 1,000° F., and for each casting temperature used, 6 different mold temperatures were used, viz.: room temperature (approximately 70° F.), 200°, 300°, 400°, 425° and 450° F., thus making 48 castings in all.

A small sized specimen was sawed from each of these pancake shaped castings for micro and macroexamination. The photo-micrographs and photo-macrographs are shown in the accompanying plates. For macroexamination the specimens were etched with brown ammonium poly-sulphide, $(NH_4)_2 S_x$, for about 30 minutes. After photographing, the specimens were repolished and etched with ferric chloride, $FeCl_3$, for microexamination. All photo-macrographs were made at 2 diameters and all micros at 100 diameters magnification.

It is obvious from these photographs that with either higher casting temperatures, or mold temperatures, or both, there is an important increase in crystal size just as might be expected. Further, that there is an important increase in the massiveness of the intermetallic compounds Cu_3Sn (needles) and SnSb (cubes). It would appear that the character of these compounds might be fairly accurately prophesied from the appearance of the macrostructure.

A representative set of the specimens was again repolished for hardness determinations. In making the hardness measurements we first tried the Rockwell machine using the 1/16 inch ball and 100 kg. load, then the ⅛ inch ball and the 100 kg. load. We then tried the Vickers machine with 1 mm. ball and 5 kg. load, and finally the microcharacter machine with a 3 g. load. In using the Rockwell and Vickers machines the average of from 5 to 8 readings was used for each specimen tried. With the microcharacter machine one scratch was made on each specimen and its width was read at 5 or 6 different places on the scratch by means of a micrometer eyepiece reading directly to microns. The micrometer eyepiece was checked against a stage micrometer.

In no case could we show any uniform change in hardness with change in crystal size. In fact, there was comparatively little difference in hardness between specimens, and the differences in hardness were of an order of magnitude which might easily have been accounted for by errors in making the determinations. It was noted, however, that the hardness of the small SnSb cubes was about the same as that of the large ones when microcharacter readings were made on them.

It was therefore decided to determine the compressive strength of a series of castings. For this purpose another set of castings was made using about the same casting and mold temperatures as before but using a different shaped casting. For making the compressive strength determinations a specimen ½ inch diameter by 1½ inches long was desirable.[1]

For these castings new metal of the same analysis was melted in a clay crucible in an electric furnace as before, but it was cast into a graphite mold about 4 inches deep, ⅝" diameter at the bottom, and ⅞ inch diameter at the top. The graphite block was 3 inches diameter by about 6½ inches long and was mounted in a sand bath. (Fig. 2.) The temperature

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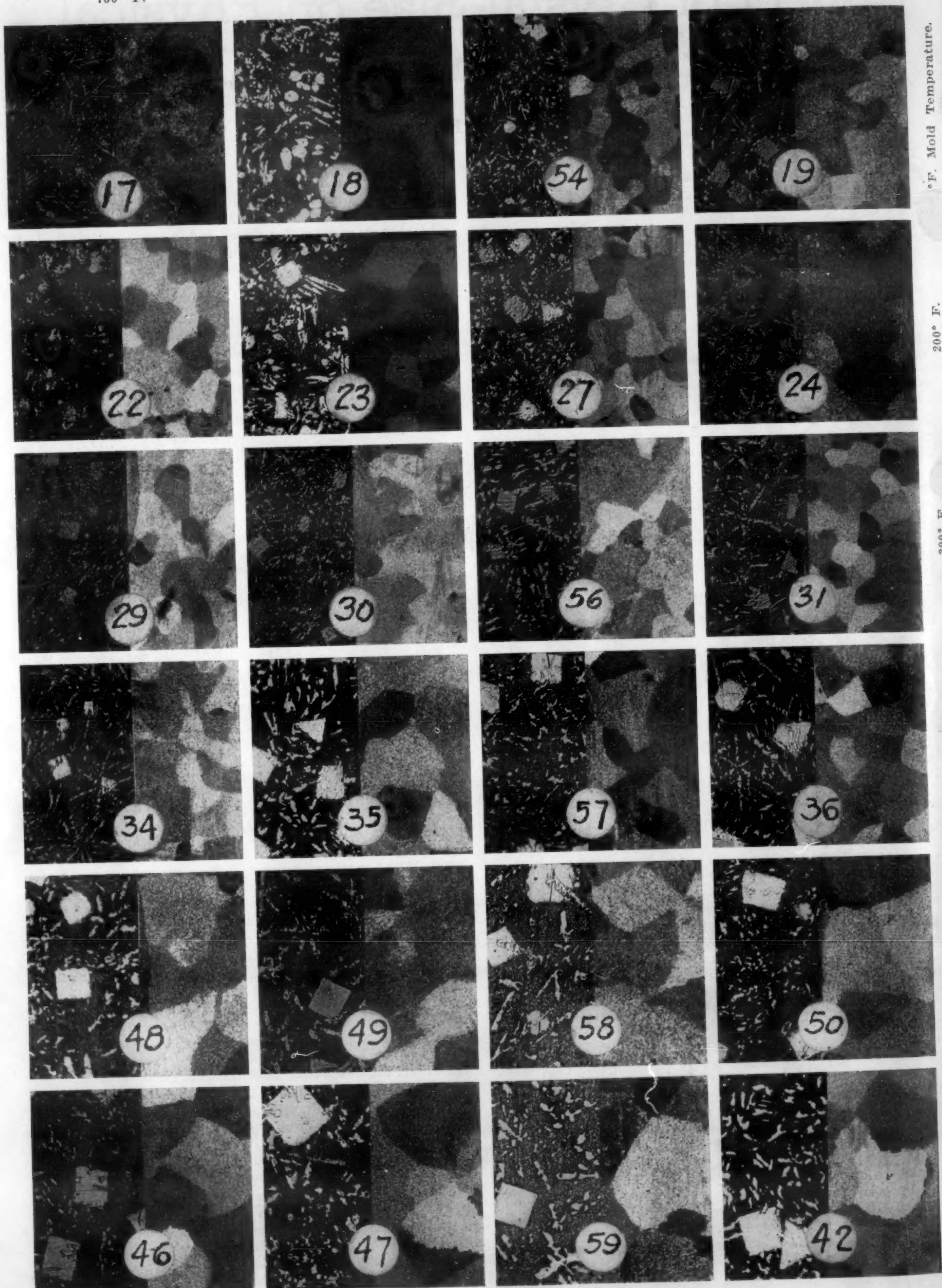
Casting Temperature

750° F. | 800° F. | 825° F. | 850° F.

°F. Mold Temperature.

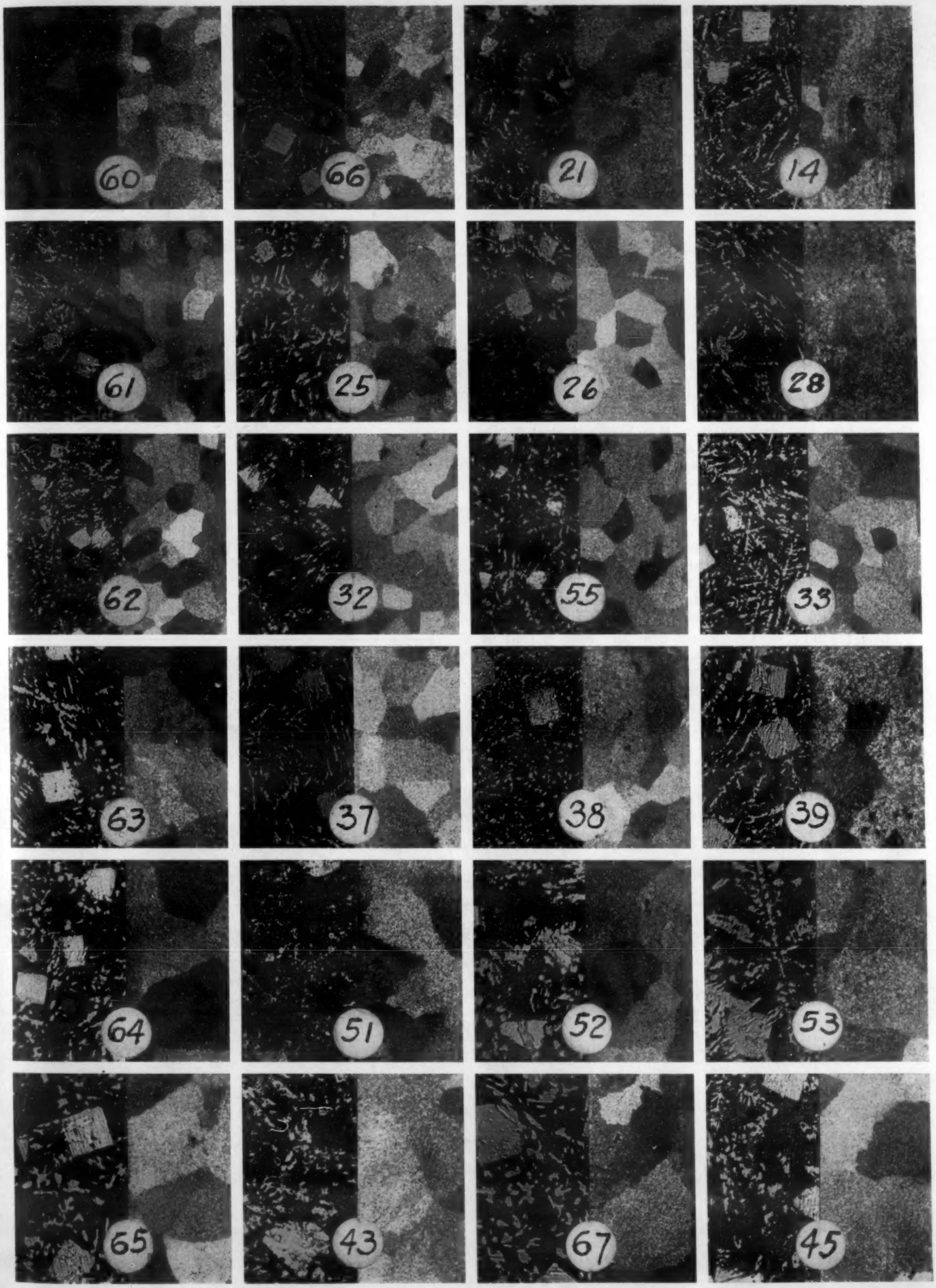


200° F. | 300° F. | 400° F. | 425° F. | 450° F.

Casting Temperature

875° F. | 900° F. | 950° F. | 1000° F.

370° F. Mold Temperature. — 200° F. — 300° F. — 400° F. — 425° F. — 450° F.



of the mold was read by means of a thermometer which read directly to 2° F., inserted well down in the mold. Until just before casting, the opening was kept closed by a plug of cotton.

The castings were generally allowed to reach room temperature before they were removed from the mold, which facilitated the removal of the castings, due to their shrinkage, as well as assuring uniformity of procedure for its effect upon the crystal size.

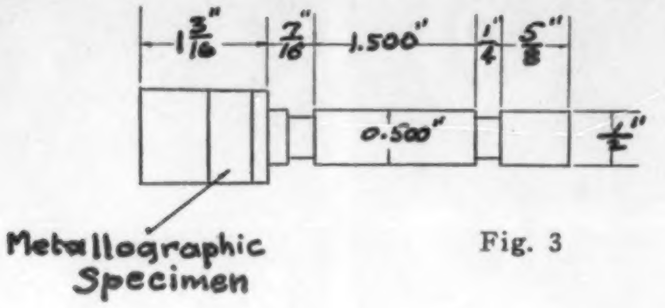


Fig. 3

These castings were then turned down to size in a lathe as shown in Fig. 3. The last 0.002" or 0.003" diameter were generally removed with Hubert papers #1 and #00. They were then cut off and the ends finished so that the faces were parallel to each other and at right angles to the main axis of the specimens by clamping them in a hardened steel fixture and polishing off the ends on a metallographic polishing wheel.

The compressive strength was determined as follows: The specimen was set into a fixture as shown in Fig. 4 and the fixture was mounted in a Southwark-Emery testing machine. The steel plunger was hardened and ground and lubricated with light oil. Its fit was close enough so that its own weight would just move it down in its bearing. An initial load of 50 lbs. was first applied and thereafter the amount of compression for each increment of 100 lbs. load applied was read from a gage which read to 1/10,000 inch, this gage being mounted on the testing machine.

These readings were continued generally until a load of 1600 lbs. had been applied with the hope that from the stress-strain curves the yield points might be determined. Freeman and Woodward[1] arbitrarily adopted the load necessary to compress the specimen 1/8% of its original length as the yield point, but our curves, Fig. 5, show no uniformity whatever when we try to apply this rule.

To determine the ultimate strength Freeman and Woodward's arbitrary rule of adopting the load necessary to produce a compression of 25% of the original length of the specimen was used.

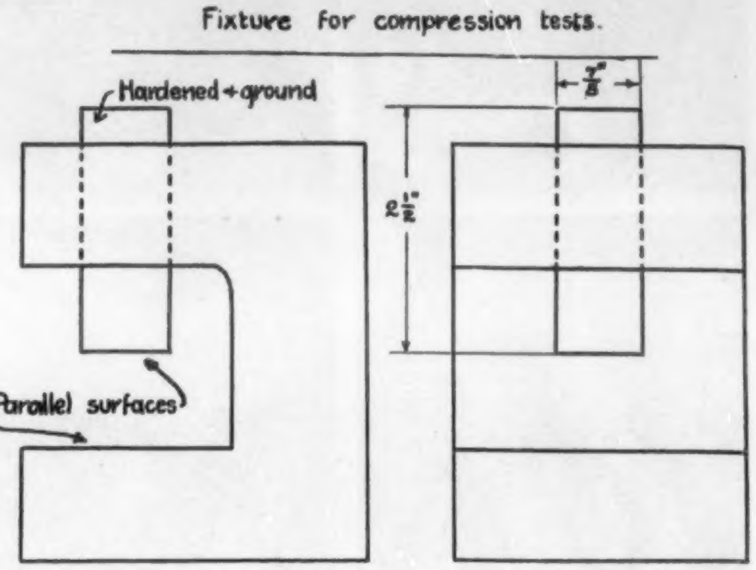


Fig. 4

To find out whether the ultimate strength varied with the crystal size only the extreme cases of casting technique were used, viz.: the 8 specimens cast from the 8 different casting temperatures into the mold at room temperature and those cast into the mold at 450° F., and the following tabulation shows that in each case the specimens having the larger crystal size showed lower ultimate strength.

Table Showing Effect of Crystal Size on Ultimate Strength

Cast'g Temp. °F.	750	800	825	850	875	900	950	1000
Mold Temp. °F.	82	86	84	82	86	82	86	83
Ultimate Strength lbs./in.^{2}	21,140	22,430	21,680	23,020	22,920	22,190	21,520	22,700
Cast's Temp. °F.	750	800	825	850	875	900	950	1000
Mold Temp. °F.	450	440	450	440	450	450	450	460
Ultimate Strength lbs./in.^{2}	18,060	19,580	17,550	18,440	19,074	18,880	16,200	16,330

[1] Freeman & Woodward. Technologic Paper 188, U. S. Bureau of Standards.

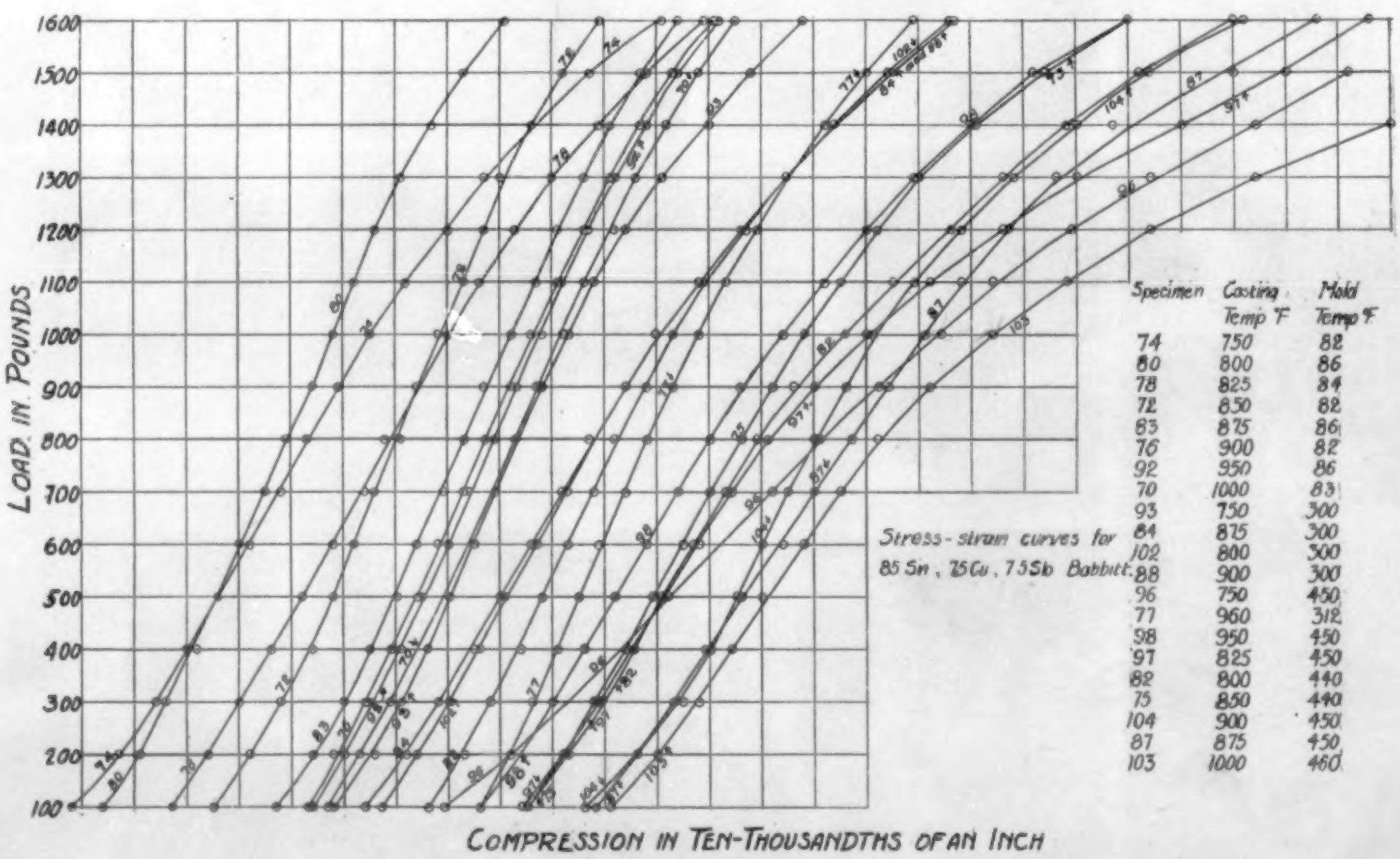
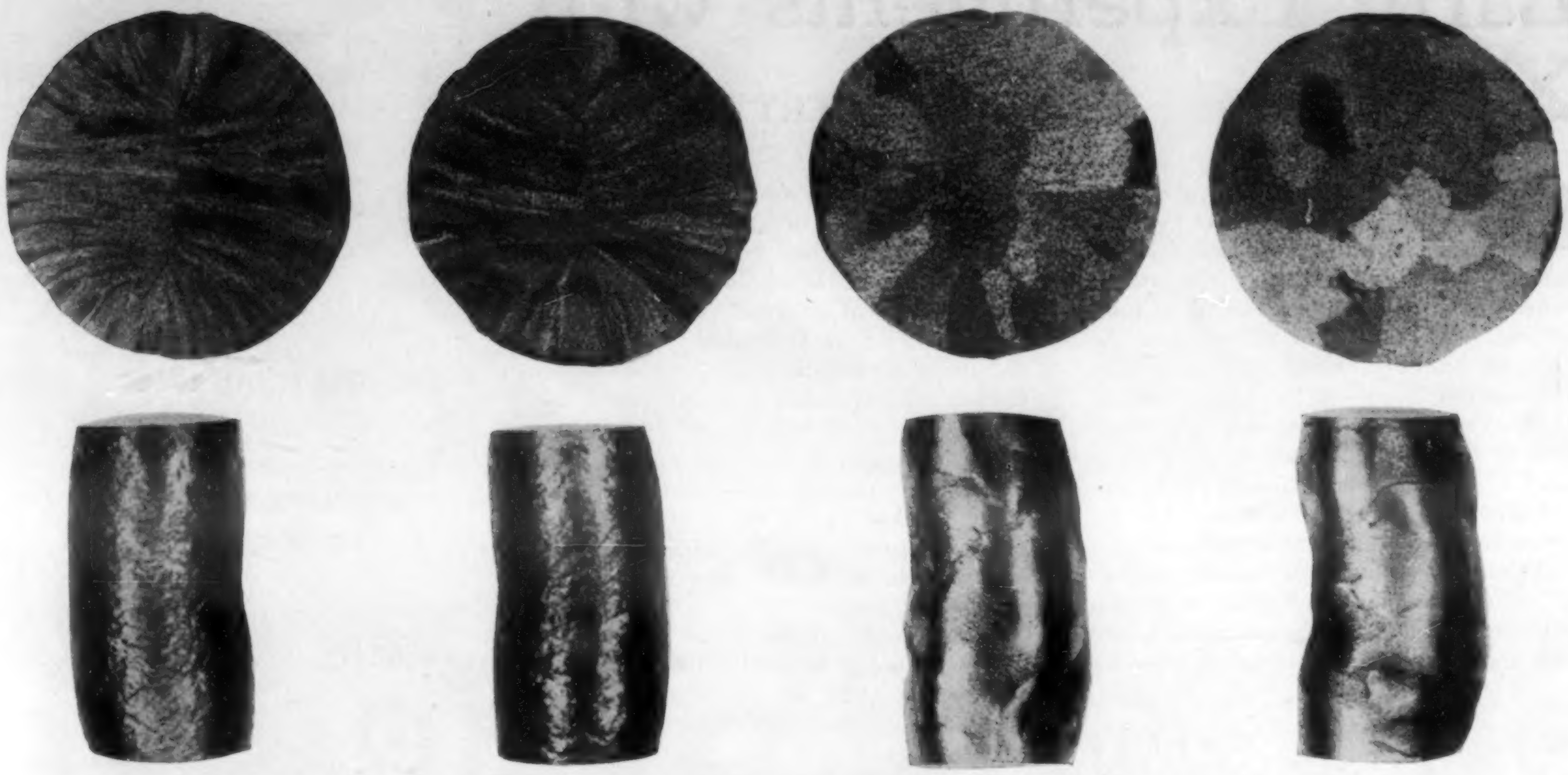


Fig. 5

BEFORE COMPRESSIVE STRENGTH TESTS



AFTER COMPRESSIVE STRENGTH TESTS

Specimen	74	83	87	96
Casting Temp. °F.	750	875	875	750
Mold Temp. °F.	82	86	450	450

Fig. 6

Five intermediate specimens were also tested and their results in general were intermediate between the high and low mold temperatures in each case.

Cast'g. Temp. °F.	750	800	875	900	960
Mold Temp. °F.	300	300	318	300	312
Ultimate Strength lbs./in.^{2}	20,760	21,430	21,170	18,370	22,070

Fig. 6 shows photographs of specimens before and after testing and it is interesting to note that the specimens having the larger crystals show large bulges on their surfaces as though the crystals had been displaced bodily when the load was applied.

From these results it appears conclusive, first, that the crystal size of babbits cast into bearings can be controlled by controlling the casting and mold temperatures; second, that hardness, as at present measured, is not a function of crystal size in tin base babbitts; third, that ultimate strength seems to decrease somewhat with increase in crystal size; and fourth, since, for a macroexamination very little preparation of the specimen is necessary, the author believes this method of investigation may prove helpful. As shown in a former paper[2] the macrostructure of a finished main, or connecting rod bearing is quickly revealed without any further preparation of the surface than the removal of the oil films.

Further problems for investigation in this field are suggested by these results such as: 1. What is the connection between crystal size and the ability of a babbitt bearing to maintain an oil film on its surface? 2. What is the connection between chemical analysis of the babbitt and crystal size? 3. Is the increase of the massiveness of the intermetallic compounds due to an increase in their amount at the expense of the tin rich ternary eutectic? Or is it due simply to an agglomeration of the finely divided material already present?

[2]*Metals & Alloys*, Vol. 2, Jan. 1931, pages 20-24.

Acknowledgments

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Alan F. Hilton, metallurgist of the Farrel-Birmingham Company, died at the New Haven Hospital, January 1932, at 38 years of age. He was a member of the American Institute of Mining and Metallurgical Engineers, the American Society for Steel Treating, member of Committee A-3 on Cast Iron and formerly a member of the Gray Iron Castings Committee of the American Foundrymen's Association.

Early Experiments with X-Rays

By ALBERT SAUVEUR

IN THE latter part of 1895 news was received from Germany that Prof. W. C. Roentgen had discovered rays capable of penetrating substances opaque to ordinary light. Being ignorant of their nature, Prof. Roentgen called them X-rays. In January, 1896—that is, a very few months later—at the suggestion of W. R. Walker (at the time General Manager of the South Works of the Illinois Steel Company), experiments were undertaken to ascertain whether by the use of such rays internal defects in steel could not be detected. My outfit consisted of a "Crookes" tube, an induction coil and a storage battery. Obviously with such crude appliances, the rays we were able to generate failed to penetrate even thin sheets of steel. That our experiments attracted public attention is evidenced from the appended photostatic reproduction of an article in the Chicago Times-Herald of February 19, 1896.

Failing to obtain results with steel, I turned my attention to a substance less resistant to penetration, namely the hand of my assistant, W. C. Post, and obtained the X-Ray picture shown in Fig. 1. I have a vivid recollection of the thrill I experienced when the bone structure of Post's hand flashed into view in the developing tray.

Fig. 1

Many other articles were exposed to X-Rays: among them the different parts of a watch (Fig. 2) placed on a photographic plate and enclosed in two cardboard boxes.

My only excuse for bringing this matter to the attention of your readers is to be found in the fact that these early experiments undertaken immediately after the announcement of the discovery of X-Rays constitute, I believe, the first attempt at applying these rays to the detection of internal defects in metals. They have, therefore, an historical interest. They also testify to the imagination and vision of W. R. Walker. In a recent book on "Metallic Inclusions in Iron and Steel," by Benedicts and Lofquist the authors write on page 161:

"Shortly after the discovery of X-Rays Feb. 1895) Albert Sauveur (at the time employed by the Illinois Steel Company) tried to use them for detecting flaws in steel. The difficulties involved in obtaining a sufficiently penetrating radiation, however, caused the experiments to be discontinued."

They write further:

"Davey (at the General Electric Company) considered the resources insufficient for obtaining results of practical importance even in 1915. It is but quite recently that X-Ray technique has advanced sufficiently to allow of a profitable application of these methods for certain purposes."

It seems evident that in January 1896, we were far ahead of our time and that we were pioneers in a field destined to yield important results.

It is also believed that the X-Ray picture of Post's hand was one of the very first such radiographs taken in the United States.

RADIOGRAPH OF PARTS OF WATCH.

Mr. Albert Sauver has taken some extremely sharp radiographs in the laboratory of the Illinois Steel Company. One of these we reproduce, showing the different parts of a watch. The sensitive plate was covered with a sheet of black paper placed in a cardboard box and the latter enclosed in another similar box. Quick plates were used, the exposure being about one and one half hours. The current was derived from a three-cell storage battery and an induction coil giving a three-inch spark was employed. The distance of the tube from the plate was five inches.

Fig. 2

FIFTEENTH YEAR.

NEW RAY ON STEEL

Roentgen System in South Chicago Rolling Mills.

CHEMIST SAUVEUR'S HOPE

Photography as a Means of Testing Metals for Flaws.

DENSITY A GRAVE HANDICAP.

Directors of Illinois Steel Company Authorize the Experiments Now in Progress.

The Illinois Steel Company is making plans to use the Roentgen photography for the detection of flaws in steel. If experiments along this line are successful one of the greatest benefits of the new photography will accrue to manufacturing and metallurgy.

Albert Sauveur, chemist and engineer of the Illinois Steel Company, is conducting these experiments. If his hypothesis is correct the penetrating nature of the ray and its photographic effects will be the means of detecting flaws in steel and determining the purity of metals. This fact is appreciated by the directors of the Illinois Steel Company and a complete and searching investigation will be made at once in the laboratory of the company at the mills in South Chicago.

Owing to the difficulty of getting the needed apparatus the experiments have been handicapped and delayed. Mr. Sauveur expects, however, to get results this week. He was fortunate in being able to obtain a Crookes tube from one of the electrical supply houses in Chicago. Besides this, he had several tubes blown at the Illinois Steel Works. He has been disappointed in securing an induction coil that will give the current necessary to produce the light.

Density of Steel a Handicap.

The chemist has been photographing various metals and has produced fair shadows. But steel is so dense that some have regarded it as doubtful if rays can be produced strong enough to pass through it and record on the sensitive plate the delicate variations in the shadows which indicate flaws.

The experiments do not differ from the numerous tests of the Roentgen discovery which are being carried on all over the country. An ordinary sensitive plate in a holder is placed beneath the Crookes tube. The objects to be photographed are placed upon the plate and the current sent through the tube to develop the unknown rays which have a photographic effect upon the plate. It has become a matter of ease now for anyone to produce shadows by metals varying in depth of tone, according to their density. It is only necessary to have a correct Crookes tube having a practically perfect vacuum. But to discover flaws in these metals by the sha[illegible] [illegible] will be much more difficult, especially when the metal is steel and almost opaque to these rays, even on long exposure. The outcome of the experiments cannot be foretold.